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Catalytic Incineration of Low Concentration Organic Vapors

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16. ABSTRACT The report gives results of a demonstration of the catalytic abatement of low concentration hydrocarbon vapors on both a pilot- and full-scale system. The tests were conducted on industrial exhausts containing CO and volatile hydrocarbons. An economic comparison was made between thermal and catalytic abatement systems, utilizing this data. The pilot-scale data was obtained over a 5-month period from a plastic printing plant where the major solvents were ethanol, n-propyl acetate, and heptane. The full-scale data was obtained over a 9-month period from a Formox (Reichold Chemical Co.) formaldehyde plant exhaust containing CO, dimethyl ether, methanol, and formaldehyde. The pilot- and full-scale units were able to convert 97-99% of the pollutants to CO_2 and water.

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Hydrocarbons	Organic Vapors	07C
Vapors	Thermal Systems	07D
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CATALYTIC INCINERATION OF LOW CONCENTRATION ORGANIC VAPORS

by

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ABSTRACT

Catalytic abatement of low concentration hydrocarbon vapors has been demonstrated. This report presents the results of the demonstration conducted on both a pilot and full-scale system. The tests were conducted on industrial exhausts which contained carbon monoxide as well as volatile hydrocarbons. Utilizing this data an economic comparison was made between thermal and catalytic abatement systems.

The pilot data was obtained in a plastic printing plant in which the major solvents were ethanol, n-propyl acetate, and heptane. Test data was obtained for a five month period.

The full-scale data was obtained from the exhaust of a Formox* formaldehyde plant. The exhaust contained carbon monoxide, dimethyl ether, methanol, and formaldehyde. Test data was gathered over a nine month period.

The pilot and full-scale units were able to convert 97%-99% of the pollutants to carbon dioxide and water.

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SECTION 1

INTRODUCTION

A study of catalytic incineration of low concentration organic vapors has been conducted. The scope of the study included both pilot-scale and full-scale demonstration testing of catalytic abatement systems. In addition to the assessment of the catalytic systems' abilities to reduce organic emissions, an economic comparison was made between catalytic and thermal air pollution abatement systems.

Catalysis is the process of changing the velocity of a chemical reaction by the presence of a substance (catalyst) that remains apparently chemically unaffected throughout the reaction.

The catalyst used in this report is a precious metal formula evenly distributed over a high surface area aluminum oxide support material. The support material comes in two forms, pellet and honeycomb. High catalyst surface area is a major contributing factor in catalyst activity in that it assists in exposing a maximum number of active catalytic sites to the flowing gas. Many catalyst formulas using platimun, palladium or other precious metals are used in combination with surface preparation to give the properties necessary for each application. Selection of a catalyst formulation and operating temperature depends on many interrelating factors. These include the organic materials to be removed, the outlet concentration to be achieved, the operating temperature, and the catalyst life which in itself is dependent on temperature, solid particles concentration in the gas and elements such as sulfur, which reduce catalyst life.

Pelletized catalyst makes for easy loading and unloading and is less expensive compared to honeycomb catalyst. It is used in pressurized chemical processes. Honeycomb catalyst with its fixed direct flow-through passages has a much lower pressure drop resulting in a smaller reactor vessel and lower power consumption by the gas moving device. Honeycomb catalyst is used

in the catalytic abatement systems.

Organic vapors as well as carbon monoxide can be removed effectively from many kinds of off-gas streams by oxidation in catalytic reactors. When the off-gases containing these pollutants are heated to suitable temperatures at a given space velocity, the combustible components react with oxygen from the air to form harmless carbon dioxide and water vapor. The term space velocity is defined as the volume of gas flowing through the catalyst per hour, divided by the volume occupied by the catalyst. Space velocity replaces the term contact time used in thermal incinerators. As a frame of reference, contact times[2] in thermal units are usually 0.3 to 0.5 seconds. A space velocity of 50,000 $hr.^{-1}$ is equivalent to a contact time of 0.072 seconds.

In a thermal incinerator, pollutants are oxidized directly in the residence chamber at high temperature-- typically above 1300°F. Because of the high fuel consumption required to maintain these temperatures in a thermal incinerator, the alternative of catalytic reaction is often preferable.

In a catalytic reactor, the catalyst induces oxidation at lower temperatures, typically at 600° - 800°F.

Lower operating temperatures mean lower fuel consumption. Lower equipment costs from smaller reactors and heat exchangers help balance the additional cost of catalyst making the overall equipment cost comparable to thermal systems.

In some cases, the heat generated by the chemical reaction within the catalytic reactor permits self-sustained operation: depending on concentration and other factors, a well-designed catalytic abatement system equipped with a heat recuperator may be self-sufficient after initial lightoff. Lower operating temperatures also have the advantage of preventing NOx formation.

The study was divided into four phases. Phase I was the process selection.

Phase II was the preparation and installation of a pilot demonstration unit on a plastic printing plant.

Phase III was a full-scale demonstration of a catalytic air pollution abatement system installed on a Formox* type formaldehyde plant.

Phase IV is this final report in which the data are presented and analyzed.

SECTION 2

CONCLUSIONS

PILOT TEST UNIT

The catalytic abatement of low level hydrocarbons from slip stream of a plastic printing press exhaust have resulted in low level emissions in that stream.

1. The catalytic abater at a space velocity of 50,000/hr^{-1} and an exhaust temperature of 315°C would reduce total hydrocarbons from the plastic printing plant 95% or more for a period of three years.
2. Increased conversion efficiency may be obtained by increasing temperature or reducing space velocity.
3. Increased catalyst life may be obtained by increasing temperature.
4. Conversion efficiency varies for the different components of the exhaust.

FULL-SCALE UNIT

The catalytic abatement system has been operating on the exhaust of a Formox* formaldehyde plant for a period of one year.

1. The removal efficiency of the catalytic abatement system has remained in the range of 97.9% to 98.5%. There is no trend in the data points which would predict a maximum catalyst life. A minimum of three to five years is indicated.
2. The catalytic abatement system was not receiving any appreciable (1 ppm) NOx nor was any NOx produced by the system.

SECTION 3

PILOT CATALYTIC UNIT

PROCESS SEARCH

As a preliminary, a search of the literature was conducted in order to identify the major industrial sources of pollution which would lend themselves to reduction by catalytic incineration. The search produced the following major categories[1] which were deemed most appropriate for an E.P.A. study.

1. Polymers and resins
2. Basic chemical manufacture
3. Chemical products manufacture
4. Evaporative loss sources

While the literature search was being conducted, Engelhard's inquiry files for the last three years were searched to find prospective test sites. A list of 68 possible test sites were identified.

PROCESS SELECTION

The list of test sites was screened to eliminate undesirable sites. Off-gas with catalyst poisons such as sulfur and heavy metals, or high solid loading, sites no longer interested or available, and systems not falling within the categories selected were eliminated. A final list of eight test sites was chosen. The companies were contacted and the program was outlined. Preliminary interest in the program was followed by visits to several test sites. Negotiations with several companies were conducted before a site was chosen.

The selection of the test site chosen was concluded on the basis of a desirable catalytic application, the interest of the company granting permission, and the facilities offered for the test program. The site chosen was

at a plastic film printing plant. The off-gas was a mixture of volatile solvents in air.

PROCESS DESCRIPTION

The test was conducted on the exhaust stream of a plastic film printing press manufactured by the Paper Converting Machine Company. It is a 6-station, 60 inches wide central impression cylinder flexographic printing press. The press contains dryers which evaporate volatile organic solvents from the plastic film after printing. (Figure 1)

The total exhaust stream from the dryers is 4.72 $m^3 s^{-1}$. Maximum exhaust gas temperature is 85°C. Drying is accomplished with two high velocity hot air impingement type dryers. Heat for the dryers is provided by two natural gas fired burners. The drying system consists of two sections: a between color dryer and main tunnel dryer. The between color dryer section partially dries each ink layer prior to the next printing station and the main tunnel dryer completes the drying sequence.

The product film is used for paper tissue packaging. The product is a reverse printed polyethylene film. Each design employs 5 to 6 colors requiring one printing station for each color.

The inks employed are solvent based polyamid printing inks which are approximately 78% by weight volatile at the proper printing viscosity. The major volatile components of the inks are ethanol, n-propyl and 2-propyl alcohol, heptane, and n-propyl and 2-propyl acetate. Ethanol is the major solvent component but the percentage of all components varies widely with different colors as does the amount of additional solvent added to the original inks to bring them to the proper printing viscosity.

PILOT TEST UNIT DESCRIPTION

The pilot test unit consists of a blower, electric heater, catalytic reactor and temperature, flow, and pressure instrumentation. A flow schematic of the unit is shown in Figure 2.

The blower draws a sample of exhaust gas from the exhaust system shown in Figure 1. Exhaust under pressure from the blower is metered through the system with a manual valve and flowmeter. An electric heater maintains the

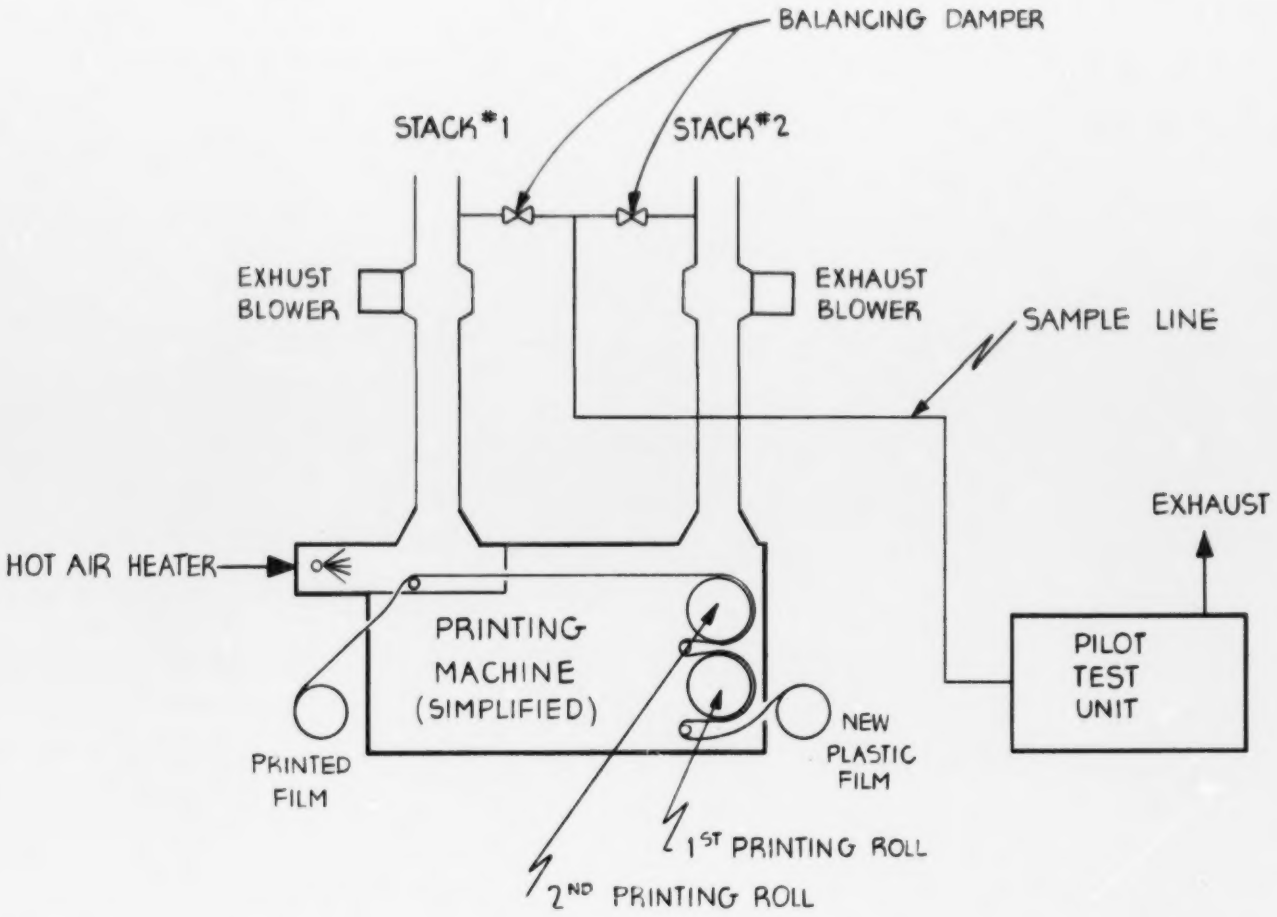


Figure 1. Flow Schematic - Printing Press/Catalytic Pilot Unit.

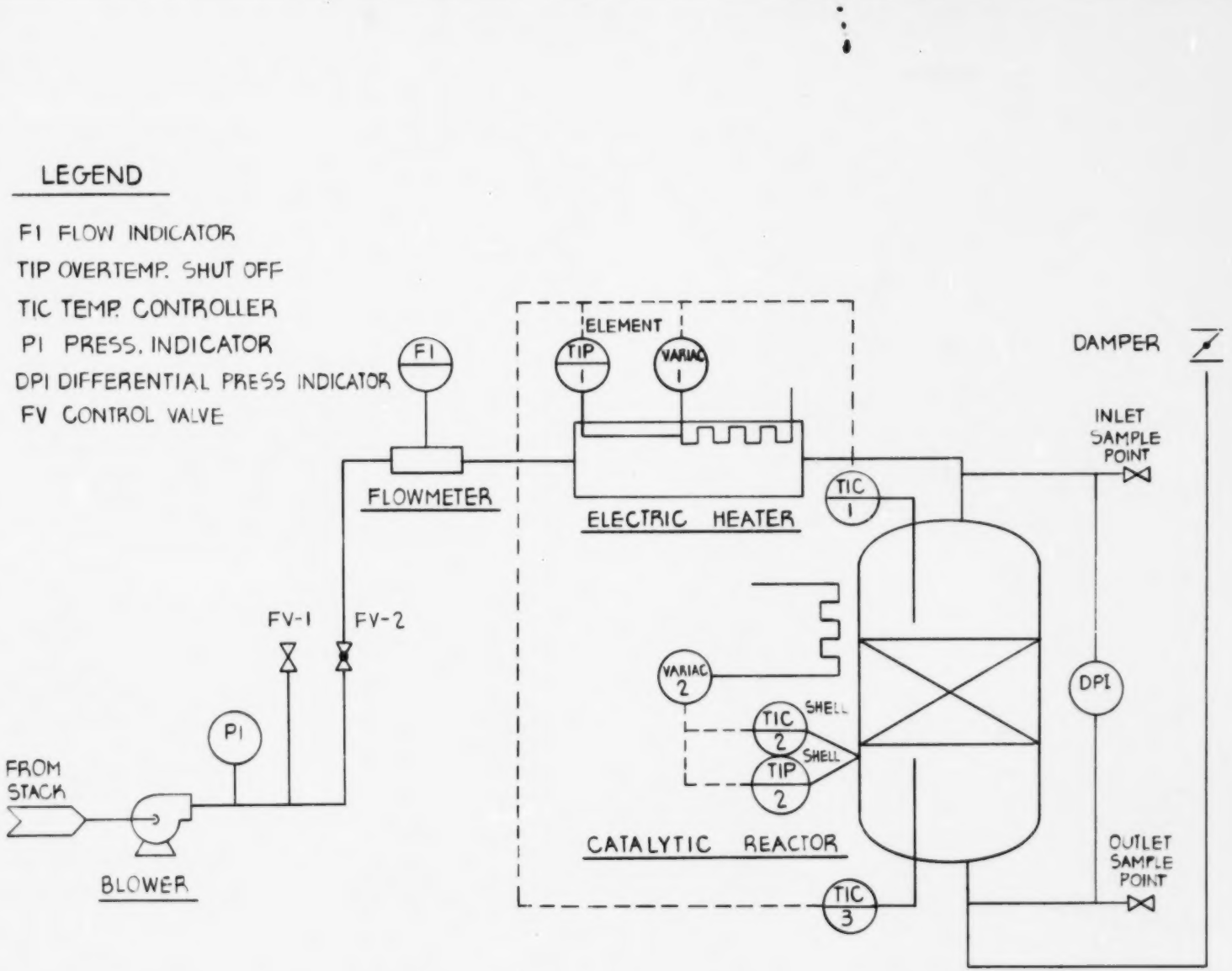


Figure 2. Flow Schematic Pilot Test Unit

exhaust at the proper temperature entering the catalyst bed. A damper on the exhaust of the catalyst bed produces a positive head throughout the system preventing leaks into the system at the sample points. The sample points are located before and after the catalyst bed. As the unit was built with English units, all descriptions in this section will be in English units to avoid confusion.

Blower

The blower is a Rotron Simplex Spiral Blower which employs the regenerative principle for moving air with a capacity of 55 SCFM at 365" H_2O. It is a Model No. SL2P2.

Flowmeter

The Teledyne Hastings Linear Mass Flowmeter is an in-line device operating on the thermal principle which depends on the mass flow of gas and its heat capacity to change the temperature along a heated conduit. The temperature change is measured at zero flow by thermocouples.

The device is calibrated for a range of 1 to 10 SCFM of air. The scale is linear. Each graduation is 0.2 SCFM. It is Model FM-42.

Electric Preheater

The electric preheater is a General Electric Calrod Circulation heater. The unit is a 4.5 KW, JG series heater with type 321 stainless steel elements. Watt density is 11 watts per square inch.

The heater elements are controlled by West Series 800 temperature controllers TIC-1 (inlet thermocouple) or TIC-3 (outlet thermocouple) via Variac No. 1. TIC-3 was selected to control thereby maintaining a fixed outlet temperature or bed temperature for all the experiments. This eliminated the fluctuations of outlet temperature caused by changes in hydrocarbon content which in turn varied the temperature rise.

Catalytic Reactor

The reactor is shown in Figure 3. The reactor contains Engelhard's proprietary catalyst. The catalyst is a precious metal formula on a unitary ceramic substrate. The Pilot Test Unit contains two catalyst elements, each 1½ inches in diameter by 3 inches deep. The total volume of the bed is 0.006 cubic feet.

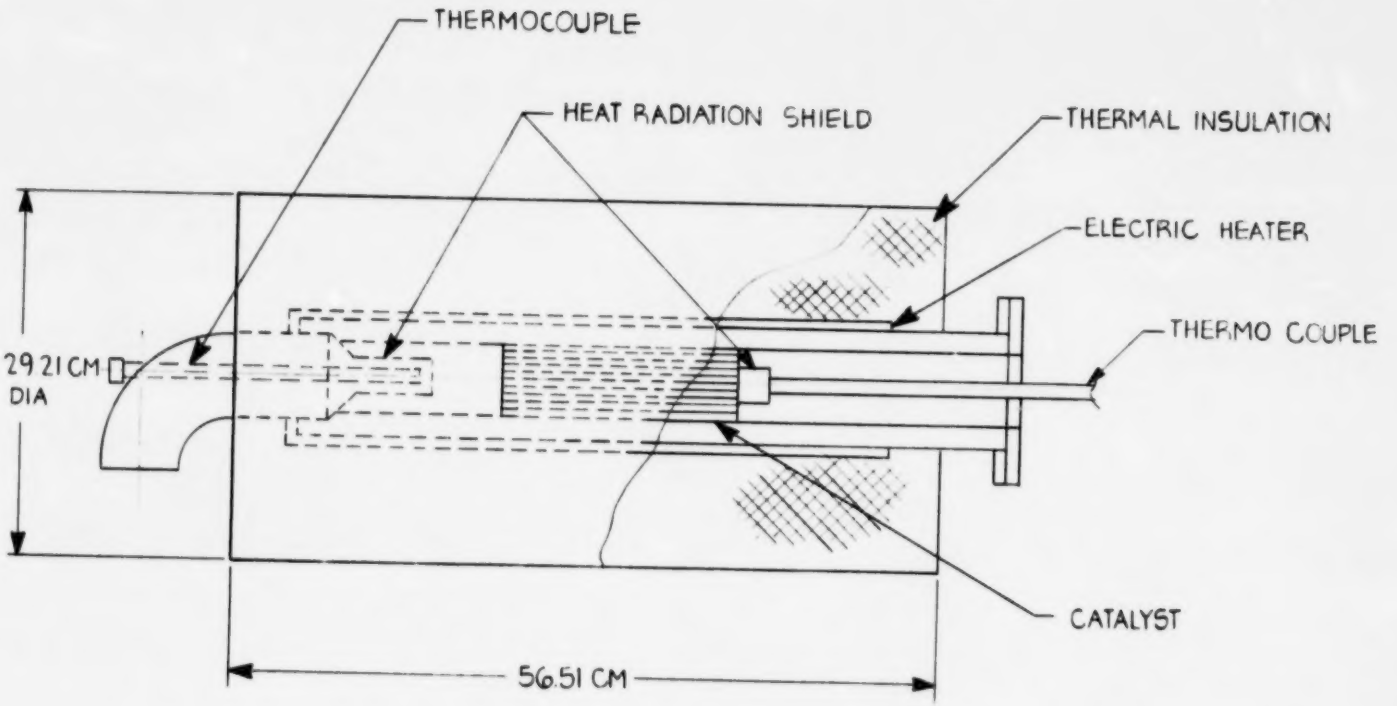


Figure 3. Catalytic Reactor

In order to properly measure the inlet and outlet temperature of the reactor, two thermocouples are furnished. The inlet thermocouple is wired to TIC-1. The tip of the inlet thermocouple is approximately 2 to 3 inches upstream of the bed. The outlet is less than one inch from the catalyst bed. The catalyst shell temperature is controlled by a temperature controller TIC-2 which controls heater elements mounted on the shell. This heater prevents heat losses from the small catalyst bed.

Thermocouples located in the air gap between the shells are wired to TIC-2 and TIP-2. While TIC-2 controls the heater elements via Variac No. 2, TIP-2 prevents the reactor shell from overheating. If a runaway reaction should occur in which the shell overheats, the unit will automatically shut down.

The reactor outlet is exhausted to the room. A damper is located on the exhaust line to control the back pressure.

PILOT TEST PROGRAM

The test program was conducted over a period of six months beginning in July and concluded in December, 1979. A total of five tests were conducted during the six-month period. The tests were all performed at three temperatures and three space velocities. A target for conversion efficiency of 95% for a three-year period was chosen. These numbers were chosen arbitrarily from past experience but proper selection of the data would make it possible to alter these numbers to meet a specific application.

During the initial testing periods, the inlet and outlet were sampled to determine the content of n-propyl acetate, ethanol and n-propyl alcohol. After testing, a comparison was made of the actual temperature rise to the calculated temperature rise. It was found that the calculated rise from the measured hydrocarbon contact was less than actual temperature rise. This indicated additional unmeasured hydrocarbon was probably present and additional testing was necessary. As a result, it was decided to also monitor total organic carbon and heptane in the exhaust. Heptane monitoring began on the September 25 test. Total hydrocarbon monitoring began on October 30.

The tests were conducted on the exhaust stream of the printing press. The printing press is used to print on polyethylene sheets and paper; however,

the pilot test was conducted only while the machine was printing on the polyethylene sheets as the paper printing had no organic solvents in the ink. During a typical 8 hour production day, the press occasionally shut down causing the temperature rise across the reactor to fall rapidly to zero. When the machine resumed printing, no test data was taken until the temperatures had stabilized so that results would be comparable with previous data. This practice was followed for test purposes only. Since the test unit was kept in operation during the down times, the reactor was immediately operable when the press resumed production. The testing was conducted at three outlet temperatures, which are 260°C, 315°C and 370°C. At each of these temperatures, data was taken at three space velocities for a total of nine data points per test. Since the velocity through the catalyst bed was extremely fast compared to the time of analysis in a gas chromatograph, it was necessary to sample the inlet and outlet simultaneously with chromatographs. This insured inlet and outlet samples of the same original composition. The sampling procedure was conducted as follows: the sample pumps were turned on to continuously withdraw the samples from the exhaust and insure a fresh sample to the instruments. When the gases had circulated for at least one minute, the samples were injected. At this point, readings were recorded from the pilot test unit for temperature, pressure and flow rate. A minimum of three samples were taken at each of the nine data points. The concentrations which are shown on the data sheets are the averages of the three chromatographic readings. For example, at a space velocity of 30,000 $hr.^{-1}$ and a temperature of 260°C, three samples were drawn to each chromatograph. For each constituent, the results were averaged to show one data point for the inlet and one data point for the outlet at each temperature and space velocity.

ANALYTICAL TECHNIQUES

For all tests, two chromatographs were employed, one dedicated to the reactor inlet and one to the reactor outlet. Chromatographs were either Carle 9700 or Varian 1200. The chromatographs were equipped with flame ionization detectors. Both analyzers were calibrated with prepared standards of ethanol, propanol, propyl acetate and heptane (when required). The

detected results were recorded on a two-pen strip chart recorder. Concentrations were then calculated.

All analysis work was conducted by Environmental Consulting and Testing Services. The analysis was performed under the supervision of J. E. Dennison, Ph.D. Details of the analytical procedures are given in Appendix C.

RESULTS AND DISCUSSION

The catalytic unit operated continuously except when the plant was printing paper. Normal operation was approximately 80% on plastic with the plant running 24 hours per day, 5 to 6 days a week. The test unit was not shut down over the weekend but ran on whatever residual material was in the press as it did during additional down periods for changeover of printing designs or press breakdowns. During these times the exhaust was essentially room air. On this basis, discounting downtimes, the actual time of abatement of the solvents was approximately 400 hours per month. Test data for the pilot test is contained in Appendix A.

A summary of the data is given in Tables 1, 2, and 3. The total removal percentage calculation is as follows:

	Inlet Concentration	Outlet Concentration
Ethanol	374	0.98
N-Propanol	194	0.41
N-Propyl Acetate	11.2	0.25
Total	579.2	1.64

$$\frac{579.2 - 1.64}{579.2} \times 100\% = 99.7\%$$

(Refer to Table A-1 Measurement No. 1 for data and Table 1 Measurement No. 1 for result.)

Three plots (Figures 4,5 & 6) show the percent conversion of hydrocarbons versus months of operation. The percent conversion is based on the total of the individual components, heptane being absent from the first two points. The three plots are for 260°C, 315°C, and 370°C exhaust temperatures. The three curves on each plot are at the three space velocities: 30,000/hr^{-1}, 50,000/hr^{-1}, and 70,000/hr^{-1}. The omission of heptane which was not

TABLE 1. Pilot Test Data Summary, Preliminary

Test	Preliminary Testing													
Date	7/17	7/17	7/17	7/17	7/17	7/17	7/17	7/17	7/18	7/18	7/18	7/19	7/19	7/19
Time	0929	1001	1030	1305	1400	1430	1500	1643	1320	1352	1515	1021	1200	1115
Measurement No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Flow Rate (m^3/h)	8.3	11.9	15.3	14.6	11.9	8.5	5.1	5.1	11.9	8.5	5.1	5.1	8.5	12.2
Space Velocity x 1000	49	70	90	86	70	50	30	30	70	50	30	30	50	72
Catalyst Inlet Temp.(°C)	371	371	371	316	316	316	313	260	266	291	277	338	346	340
Catalyst Outlet Temp. (°C)	402	406	407	360	362	362	360	316	316	313	311	354	371	368
Catalyst Press. Drop (Pa)	622	846	1120	996	871	572	373	249	747	498	249	249	498	747
Removal %														
Ethanol	99.7	99.6	99.6	99.6	99.6	99.6	99.8	99.6	98.6	99.0	99.8	99.8	99.4	98.9
N-Propanol	99.8	99.8	99.4	99.1	99.2	99.6	99.9	99.8	98.7	99.3	99.9	99.8	99.6	99.1
N-Propyl Acetate	97.8	97.8	93.1	94.6	97.1	97.2	99.4	97.5	99.4	92.2	97.7	94.4	97.7	90.8
Total	99.7	99.6	99.4	99.3	99.4	99.5	99.8	99.6	98.6	99.0	99.8	99.7	99.4	98.9

TABLE 2. Pilot Test Data Summary, Months One and Two

Test	One Month									Two Month								
Date	8/15	8/15	8/15	8/15	8/15	8/15	8/16	8/16	8/16	9/17	9/17	9/17	9/18	9/18	9/18	9/18	9/18	9/18
Time	1221	1301	1346	1542	1614	1642	1112	1138	1303	1420	1445	1545	0925	0957	1005	1208	1253	1357
Measurement No.	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1	12.1	8.5	5.1	11.7	8.5	4.9	11.7	8.5	5.1
Space Velocity x 1000	70	50	30	70	50	30	70	50	30	71	50	30	69	50	29	69	50	30
Catalyst Inlet Temp(^oC)	327	327	333	230	232	227	285	288	282	337	335	326	285	288	285	232	229	241
Catalyst Outlet Temp(^oC)	365	368	368	260	260	260	316	316	316	371	371	371	316	316	313	260	263	257
Catalyst Press. Drop(Pa)	747	622	373	622	373	249	747	498	249	747	809	373	747	498	249	622	373	249
Removal %																		
Ethanol	98.8	99.2	99.7	99.4	99.4	99.8	98.4	98.8	99.8	99.4	99.5	99.9	98.2	98.9	99.3	96.9	98.1	99.7
N-Propanol	99.0	99.4	99.8	98.0	99.1	99.7	96.5	97.8	99.6	99.7	99.9	99.9	97.9	98.8	99.4	97.0	97.2	99.8
N-Propyl Acetate	95.1	97.8	99.8	58.6	68.3	82.0	91.7	94.5	99.2	96.5	99.0	99.6	93.5	95.8	99.1	54.8	59.8	93.3
Heptane	-	-	-	-	-	-	-	-	-	96.9	97.3	97.6	88.1	84.0	98.0	34.7	58.0	92.7
Total	98.7	99.2	99.7	97.0	98.2	99.1	97.4	98.3	99.7	99.5	99.6	99.9	97.8	98.9	99.3	95.1	95.9	99.4

Table 3. Pilot Test Data Summary, Months Three & Five

Test	Three Month									Five Month								
Date	10/10	10/10	10/10	10/11	10/11	10/11	10/11	10/11	10/11	12/11	12/11	12/12	12/12	12/12	12/12	12/12	12/12	12/12
Time	*	*	*	*	*	*	*	*	*	1458	1615	1019	1117	1230	1318	1453	1515	1540
Measurement	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1
Space Velocity x 1000	70	50	30	70	50	30	70	50	30	70	50	30	70	50	30	70	50	30
Catalyst Inlet Temp.(^oC)	337	337	327	279	285	271	238	230	232	330	330	319	260	260	252	221	224	221
Catalyst Outlet Temp (^oC)	371	371	362	316	316	316	266	260	260	371	371	365	321	319	319	260	265	260
Catalyst Press. Drop(Pa)	647	498	299	647	498	249	622	373	249	560	436	249	498	373	249	436	324	199
Removal %																		
Ethanol	98.3	99.1	99.8	97.2	98.0	99.7	95.7	97.6	99.7	98.7	99.5	99.8	97.8	98.9	99.7	96.0	97.5	99.6
N-Propanol	99.9	99.9	99.9	96.3	97.3	99.8	95.0	97.2	99.7	98.6	99.5	99.8	97.3	98.8	99.8	95.5	97.5	99.8
N-Propyl Acetate	96.2	99.6	99.7	86.5	93.0	98.5	52.9	51.0	61.5	96.2	99.8	99.8	85.0	93.1	99.0	44.2	59.6	78.0
Heptane	-	-	-	83.3	63.8	97.7	57.7	62.0	78.0	-	-	99.0	85.3	91.9	98.3	24.1	50.4	77.0
Total	98.8	99.5	99.9	96.2	97.3	99.6	93.0	95.9	98.9	98.5	99.5	99.8	96.9	98.5	99.7	90.7	94.0	97.9
Total Organics**	97.7	98.0	98.0	94.3	95.0	95.2	82.6	85.8	87.5									

*Average of three or more tests.

**As analyzed. See data section.

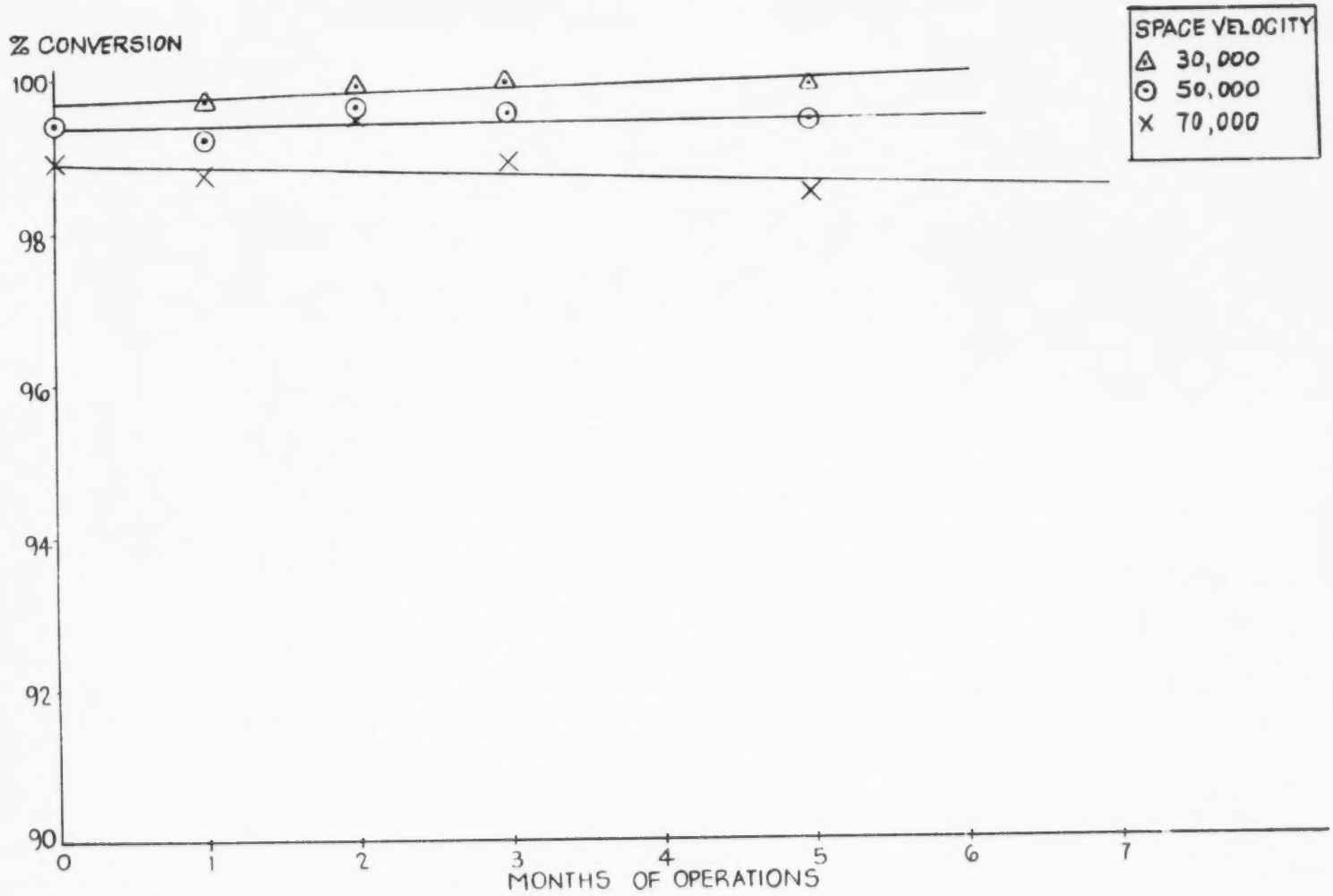


Figure 4. Effects of Time and Space Velocity on Conversion Efficiency of Total Hydrocarbons at 370°C

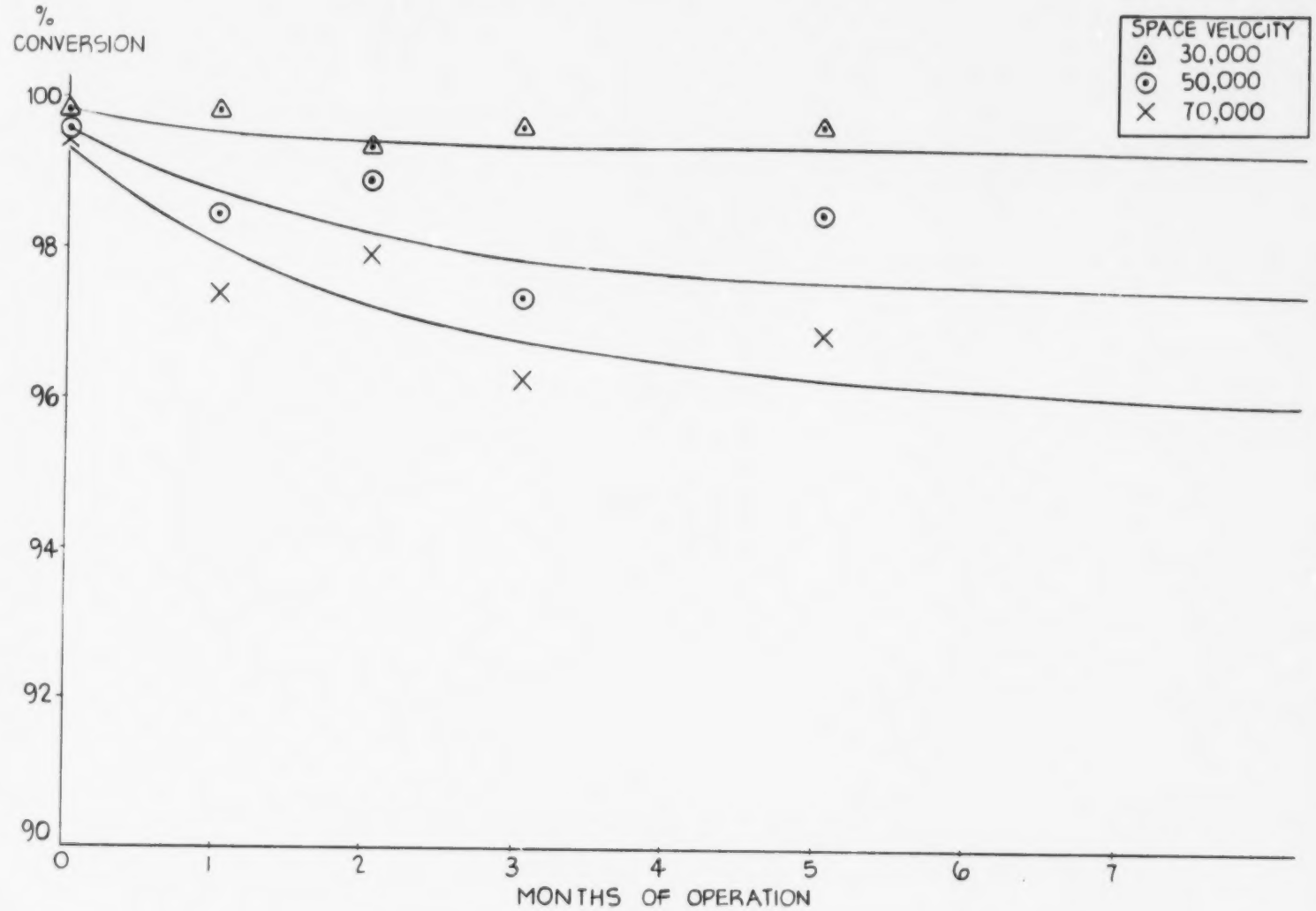


Figure 5. Effects of Time and Space Velocity on Conversion Efficiency of Total Hydrocarbons at 315°C

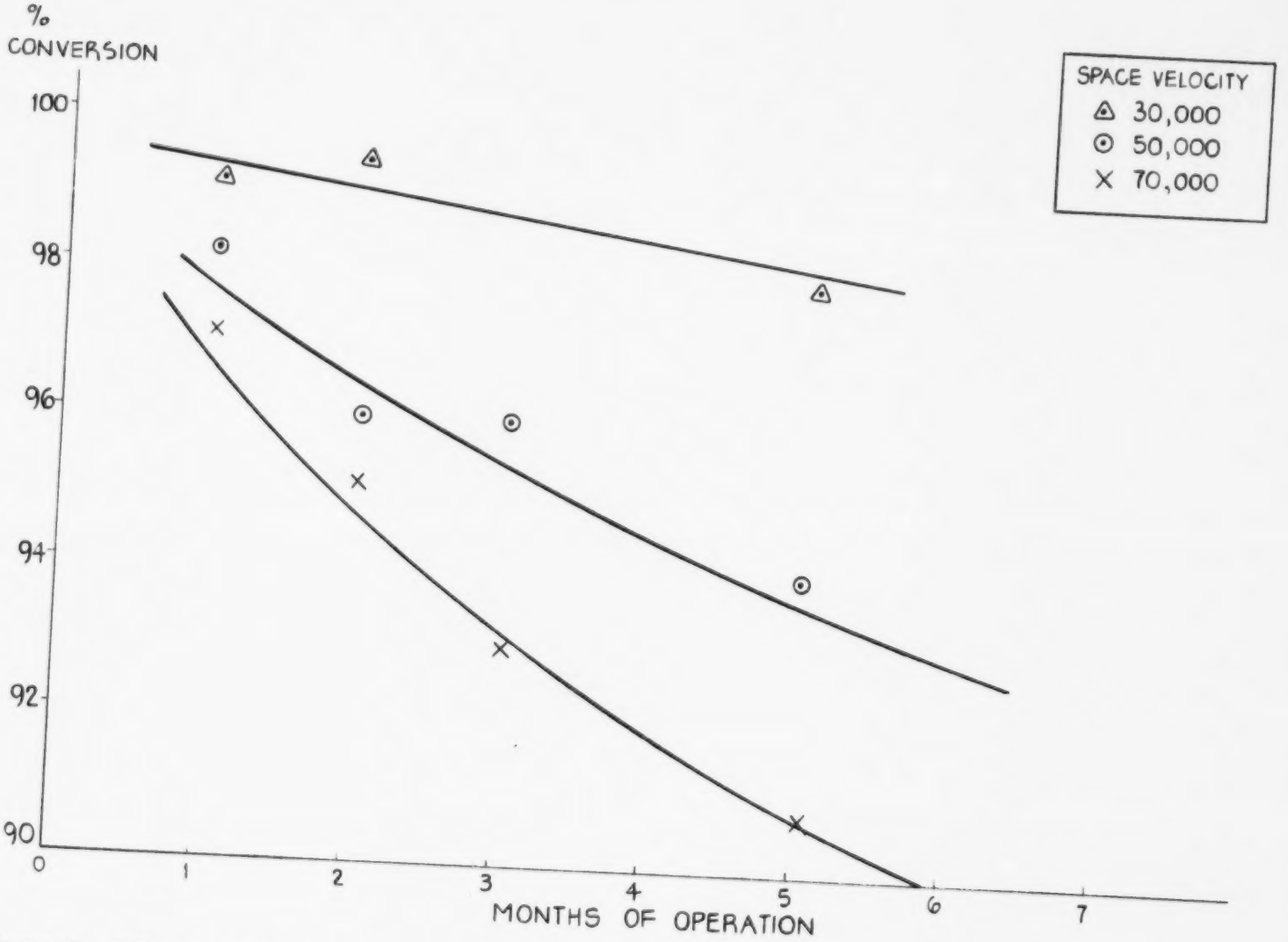


Figure 6. Effects of Time and Space Velocity on Conversion Efficiency of Total Hydrocarbons at 260°C

originally in the analysis has little effect on the overall conversion efficiency as it is only 2% or 3% of the total organic content.

If a conversion efficiency of 95% over a three year period were to be chosen as the basis of a full-scale design the curves plotted in Figures 4, 5, and 6 would help to determine the minimum space velocity and temperature. It is evident from Figure 6 that at 260°C none of the data would provide a 95% conversion for three years. Even at a space velocity of $30{,}000/hr^{-1}$ the slope of the line is approximately -0.275% per month which amounts to a 10% reduction in conversion efficiency. The slope was determined as

$$\text{slope} = \frac{\%\ \text{conversion month 5} - \%\ \text{conversion month 1}}{4\ \text{months}}$$

In Figure 4 there is no slope to the curves for space velocities at $30{,}000/hr^{-1}$ and $50{,}000/hr^{-1}$ at 370°C. This means the catalyst at these conditions has an indeterminate life beyond anything predictable. At a space velocity of $70{,}000/hr^{-1}$ and 370°C the slope of the curve is approximately -0.06% per month which amounts in 3 years to a 2% reduction in conversion efficiency from an initial efficiency of 99%. This easily meets the criteria.

At a temperature of 315°C, Figure 5, the slope of the $30{,}000/hr^{-1}$ space velocity curve is indeterminate predicting it would again meet the criteria. At $50{,}000/hr^{-1}$ space velocity the slope is approximately -0.1% per month after the first three months. Adding the slope to the value at the end of three months gives an approximate conversion percentage of 94.5% at the end of 3 years. At $70{,}000/hr^{-1}$ space velocity the conversion would be much less than 95%.

Additional individual component plots were drawn (Figures 7 & 8) of n-propyl acetate and heptane which are more difficult to oxidize. This was done to accentuate the differences in percent conversion of organics at varying temperatures and space velocities. Figure 7 is a plot similar to Figures 4, 5, and 6, but is for n-propyl acetate only. Being more difficult to oxidize than the two alcohols, the trend of the curve is easier to identify. Fortunately, the data are quite regular and provide smooth curves. Repeating this procedure for heptane component (Figure 8), was not as satisfactory, but the general position of points is similar to the n-propyl acetate. These two components combined make up less than 10% of the total pollutants

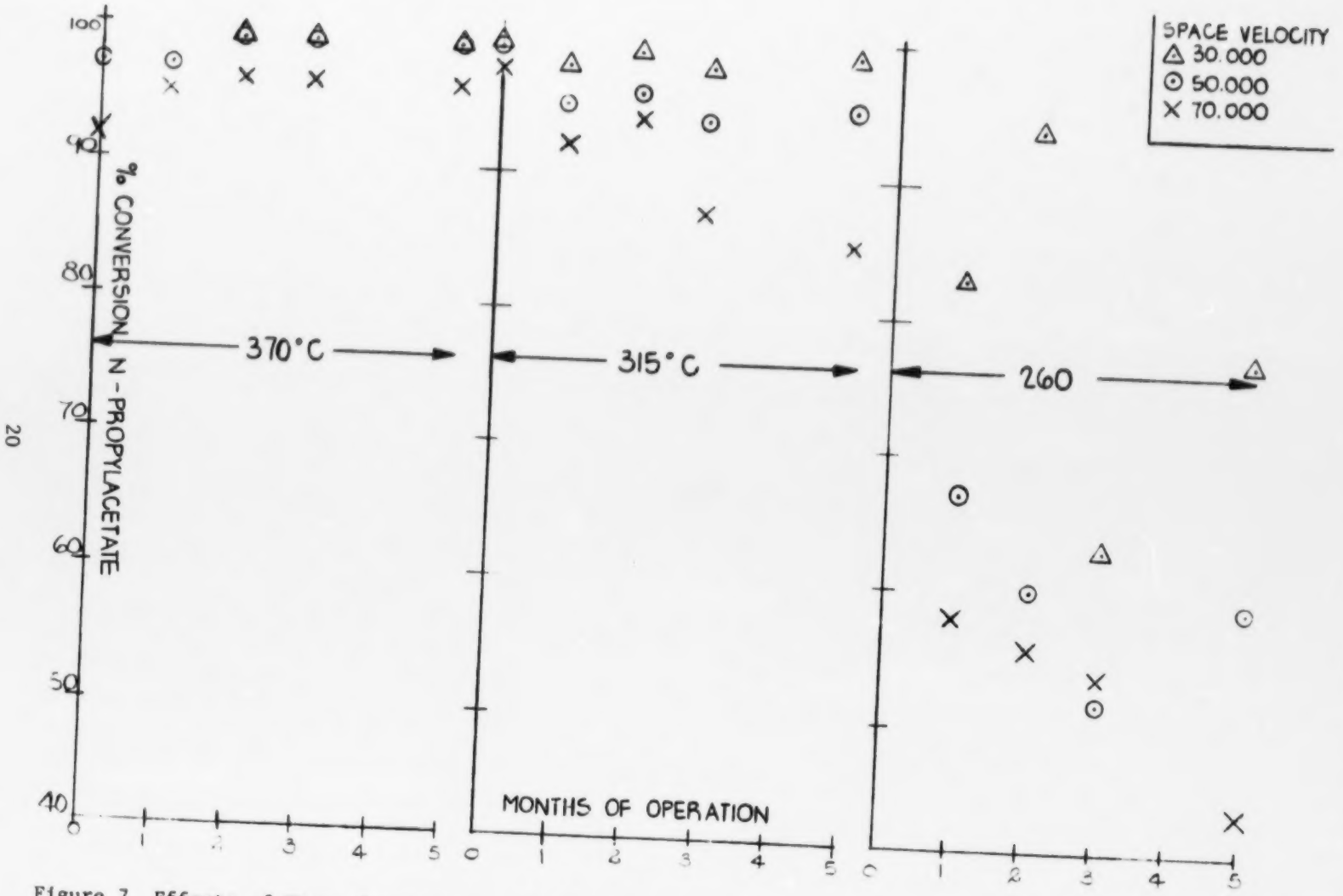


Figure 7. Effects of Time, Temperature, and Space Velocity on Conversion Efficiency of n-Proply Acetate

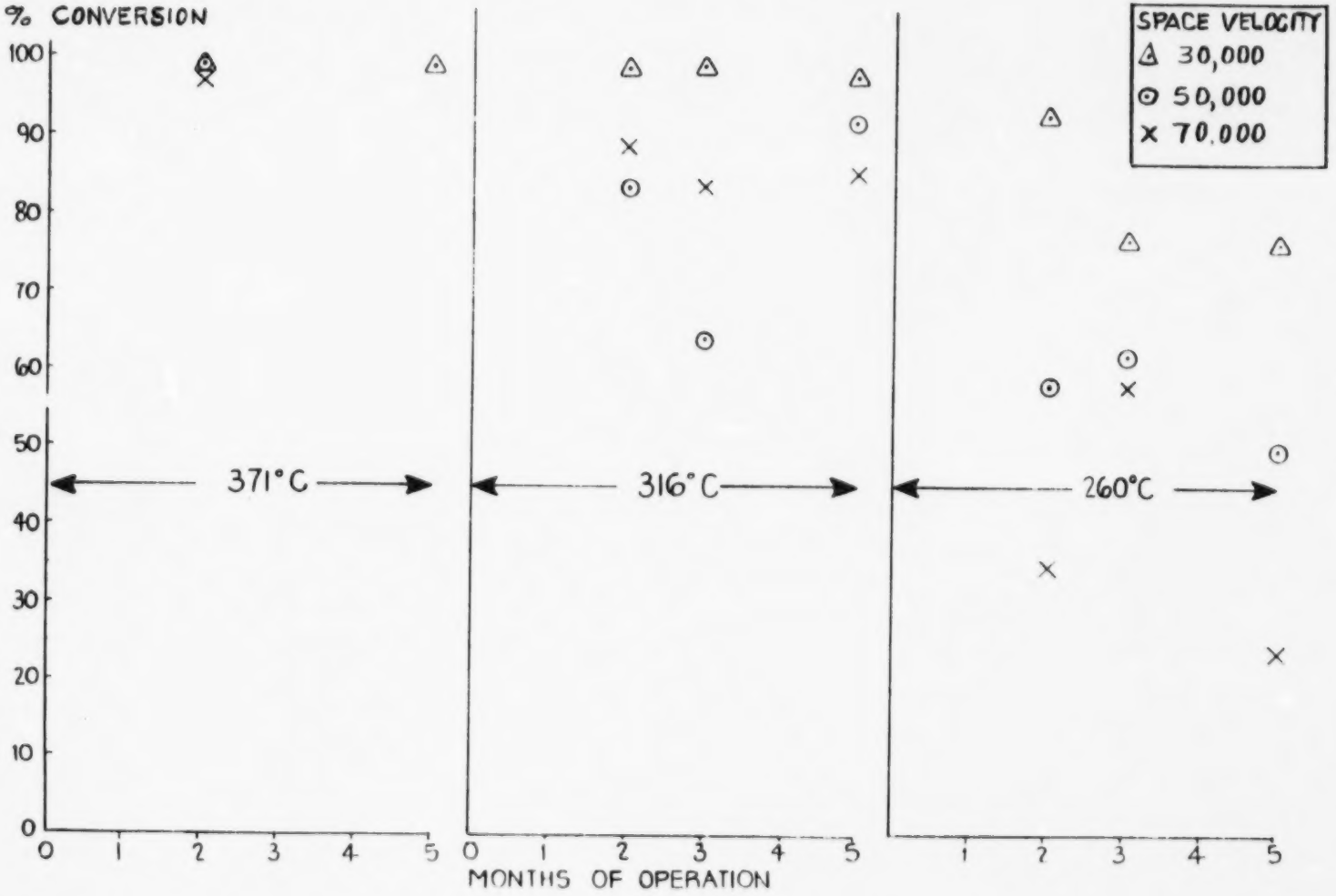


Figure 8. Effects of Time, Temperature, and Space Velocity on Conversion Efficiency of Heptane

and, therefore, do not affect the overall conversion to a large degree.

It should be noted that the initial eight data points are not shown in any of the data plots. These points were taken on start-up to determine the operating parameters. In addition, the temperature parameter at 260°C was not determined to be necessary until after the first month's testing was complete.

An additional test was conducted at the end of the fourth month. This was an analysis for total hydrocarbons using hexane as the standard. Results on the basis of conversion efficiency closely paralleled the values obtained from using the total of independent components, but at somewhat lower efficiencies. A review of the chromatographic recordings when testing for the individual components did not reveal any substantial curves to indicate a quantity of unknown compounds which might explain the lower conversion efficiencies.

SECTION 4

FULL SCALE CATALYTIC UNIT

INSTALLATION

The full-scale unit is an Engelhard Deoxo Catalytic Pollution Abatement System, Model PAS-4, installed on a formaldehyde plant using the Formox* process under license from Reichhold Chemicals, Inc. (Figure 9). The process makes formaldehyde by passing preheated air and recycled process gas mixed with methanol through a Formox* catalyst. The reaction without balancing the equation is

$$\underset{\text{methanol}}{CH_3OH} + \underset{\text{oxygen}}{O_2} + \text{inerts} \longrightarrow \underset{\substack{\text{formal-}\\\text{dehyde}}}{HCHO} + \underset{\substack{\text{dimethyl}\\\text{ether}}}{CH_3OCH_3} + \underset{\substack{\text{carbon}\\\text{monoxide}}}{CO} + \text{inerts}$$

Recycling takes place with sufficient air addition to keep the inlet oxygen level at about 10%. It is, therefore, necessary to withdraw approximately 25% of the exhaust gas to remove the inerts, i.e. nitrogen, dimethyl ether and carbon monoxide.

The catalyst is contained in a multiple tube converter where a controlled reaction takes place. Formaldehyde is absorbed in multiplate columns which produce an essentially methanol-free product.

PROCESS DESCRIPTION

The catalytic incinerator (Figure 10) is used to reduce hydrocarbon emissions being exhausted in the off-gas from a Formox* formaldehyde plant. The gas stream, under saturated conditions, exits the plant at a rate of 4500-6000 m^3/h entering the catalytic incinerator at 32-43°C. The entering gas passes through a gas-to-gas recuperative heat exhanger to raise the temperature to 232°C minimum. The gas then proceeds through a gas-fired preheater which is used to start the system or add heat if the incoming exhaust

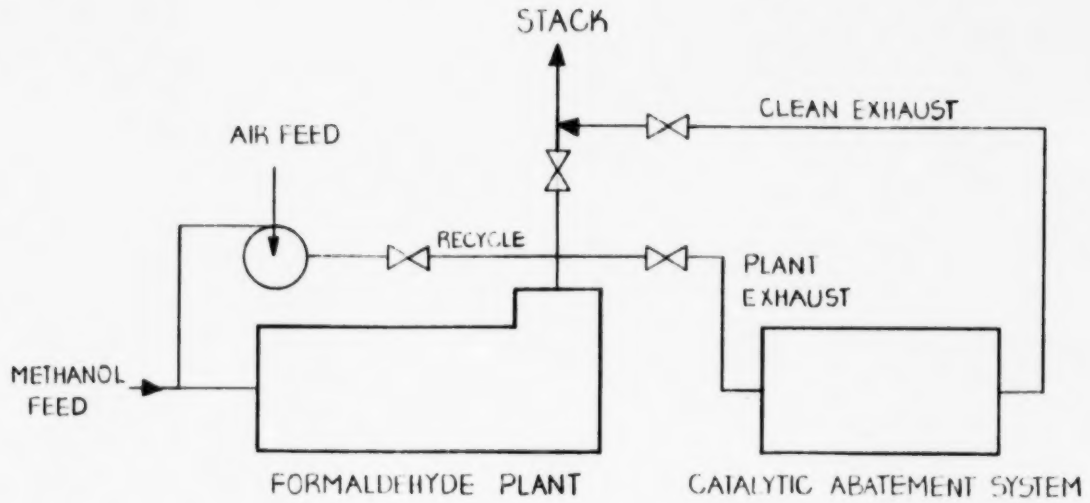
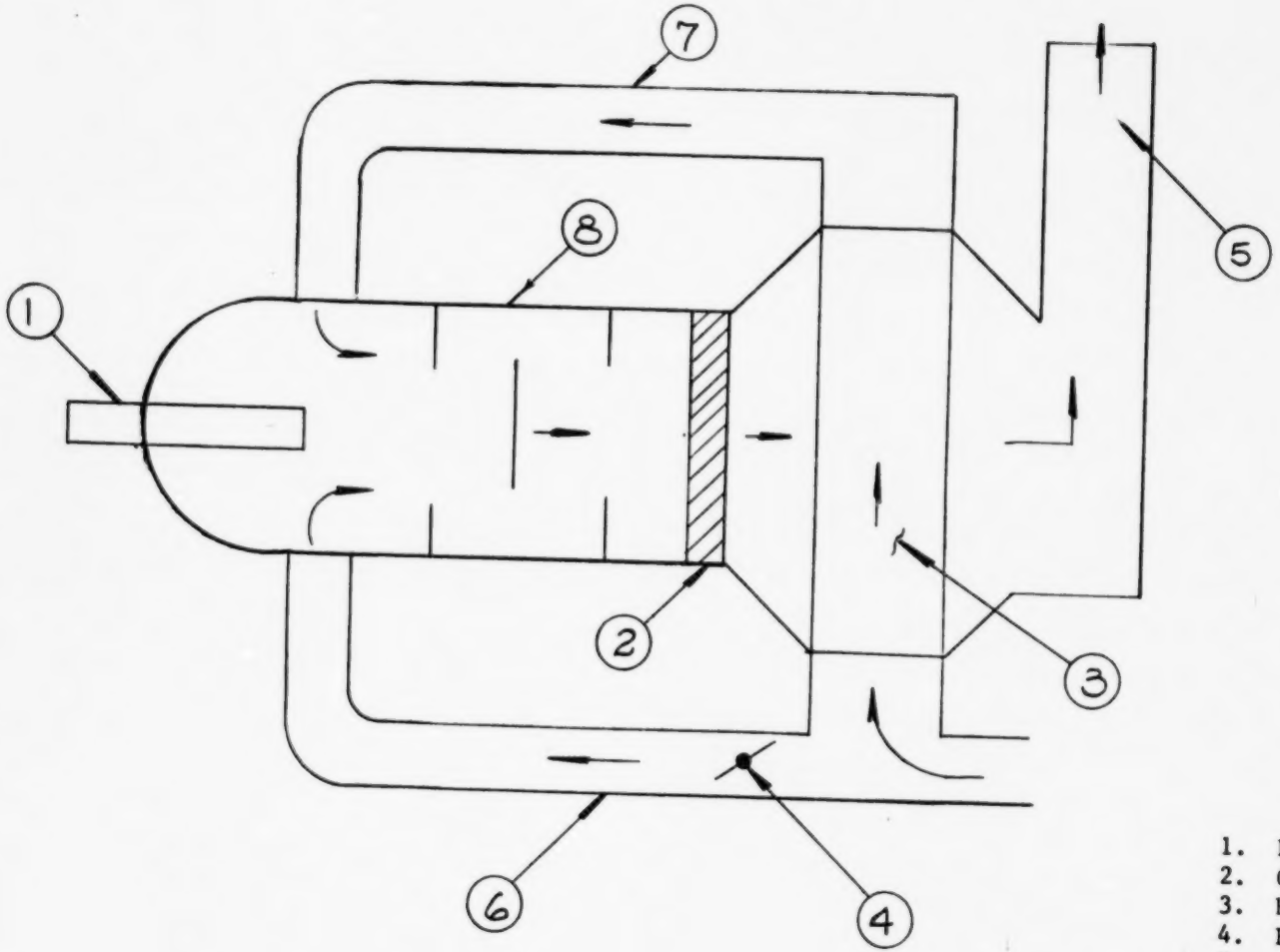


Figure 9. Flow Schematic Formaldehyde Plant/Catalytic Abatement System



1. Burner
2. Catalyst Bed
3. Heat Exchanger
4. Bypass Valve
5. Stack
6. Bypass Duct
7. Warm Gas Duct
8. Mixing Section

Figure 10. Full Scale Catalytic System

is low in heat content. It then passes through a mixing section to assure even distribution of the heat before entering the catalyst bed. After combustion, the temperature rises to 427-621°C, depending on hydrocarbon loading, the hot exhaust gas passes through the heat exchanger to the exhaust stack. A bypass of the inlet gas around the heat exchanger permits regulation of the incoming gas stream temperature.

The exhaust stream inlet has the following composition**:

Carbon Monoxide	3000-8000 ppm
Methanol	100-900 ppm
Dimethyl Ether	2500-4500 ppm
Formaldehyde	50-500 ppm
Nitrogen	90-92%
Oxygen	6-7%

FULL SCALE UNIT DESCRIPTION

The Engelhard Deoxo Catalytic Pollution Abatement System, Model PAS-4 (Figure 10) includes a catalytic reactor, heat exchanger, burner system, mixing section, and instrumentation for proper operation.

Exhaust enters the system below the heat exchanger and proceeds through the heat exchanger or bypasses it before going to the mixing section where additional heat may be added. After mixing thoroughly to assure a uniform reaction, it passes through the catalyst bed exiting into the heat exchanger and up the stack.

Catalytic Reactor

The reactor contains Engelhard's proprietary precious metal formula on a honeycomb ceramic substrate. The substrate is in block form and is layered between stainless steel wire supported by a stainless open grating.

Heat Exchanger

The inlet gas is preheated by passing vertically inside the tubes of the heat exchanger. A bellows seal on the tube side prevents leakage of untreated exhaust gas to the clean exhaust side. The hot clean exhaust from the catalyst bed passes horizontally through the heat exchanger to preheat

**On a dry basis. Actual gas is saturated at 25°-38°C.

the incoming untreated exhaust. The heat exchanger is constructed of Type 304 stainless steel tubes and a carbon steel shell which is internally insulated.

Burner System

The burner system consists of a blower to furnish combustion air, a gas train, a modulating air valve, a burner, an ultraviolet flame sensor, and a supervisory panel to control the burner system. The burner system is a complete package designed to meet the insurance requirements for burner safety i.e., flow switches, purge cycles and flame sensing.

Mixing Section

The mixing section of the unit was designed to blend the incoming gas stream with the hot gases from the burner system or to blend hot and cold incoming exhaust when the bypass is functioning. In addition, it supports the catalyst bed allowing it to expand and contract through a slip joint into the conversion section attached to the heat exchanger. The burner is mounted at the inlet to the mixing section. The total unit is externally insulated and weatherproofed.

Instrumentation

Control of the exhaust flow through the system is by means of manual valves and is external to the abatement system. Operation of the system therefore is restricted to controlling temperatures and alarming if the system goes out of control.

Four temperature indicator controllers are on the system. The first is placed before the catalyst bed to monitor incoming temperature. The second unit controls the burner system modulating the gas stream to a temperature of 440°-450°C. In addition it will shut the burner system down completely above that temperature. Under normal operating conditions the system will float above 450°C but below 565°C without control. If the temperature goes above 565°C a third temperature control will open a bypass valve which allows the exhaust to bypass the heat exchanger and reduce the inlet temperature. A fourth controller is an overtemperature unit which will shutdown the burner system if it has continued to operate by a malfunction. It will also sound an alarm so that the operators will know that the temperature in the system has reached a level where the total system should be corrected or bypassed.

This part of the control requires manual reset.

TEST PROGRAM

The test program began in July, 1979, and has now become a part of a continuous monitoring system of the process. The program was conducted so that samples were obtained once or twice a week. Each test reading is an average of two samples. Grab samples were used on both the inlet and exhaust from the abatement system. Difficulty in separating the hydrocarbon components in the packed columns of the gas chromatograph prevented acceptable data from being obtained until October so that the program was extended until February, 1980, to achieve a six-month program.

Testing on the full-scale system as compared to the pilot systems was restricted. Very little variation of temperature or flow was obtained as the system was abating a plant under steady state conditions. Minor variations in feed conditions and plant operating conditions did vary the inlet pollutant concentrations as shown in the data. Within these ranges, little or no effect was found in the outlet or abated concentrations.

As an additional part of this program, a one day test was conducted to determine the NOx level in the exhaust stream.

ANALYTICAL TECHNIQUES

All testing used grab sample techniques and the analysis was by gas chromatography. This work was carried out by plant personnel and is detailed in Appendix D-1. This includes a discussion of quality control.

An exception to the above was the NOx test which was conducted by Environmental Consulting and Testing Services using the chemiluminescence technique. This technique is described in Appendix D-2.

RESULTS AND DISCUSSIONS

Operation of the catalytic incinerator has been, with minor exceptions, reasonably constant from July, 1979, until March, 1980. Flow rate through the system averaged 5211 m^3/h with a high of 5709 m^3/h and a low of 4588 m^3/h except for a two week period in January when it averaged 3093 m^3/h. Inlet temperatures averaged 241°C with a high of 271°C and a low of 195°C while

outlet temperatures averaged 536°C with a high of 571°C and a low of 430°C. Complete test data for the full-scale unit is contained in Appendix B.

Analytical problems both at the beginning and end of the testing prevented a uniform set of data from being taken. Initially, the carbon monoxide readings of the outlet analysis were found to be greatly influenced by the absorption column of the chromatograph. This was corrected in the latter part of October. Data for this questionable period on carbon monoxide outlet is not given. Data for inlet and outlet analysis for formaldehyde and methanol increased unreasonably after mid-January. Subsequent investigation showed that part of the absorption media was blown out of the column with particles carried over into the chromatograph. After installation of a new column, and a recalibration of the unit, it was found that the formaldehyde was 14 ppm and the methanol was 6 ppm in the outlet stream.

Complete data was obtained for November 30, December 18, January 11, and March 13, 18, and 25. Conversion efficiencies for these dates were 97.9%, 98.5%, 98.3%, 97.9%, 98.3 %, and 98.0%. Refer to Summary Table 4.

A study of the inlet data from November through February, shows values that are typical of a Formox* type plant. Values for CO range from 3390 ppm to 8050 ppm, dimethyl ether ranged from 2420 ppm to 5150 ppm, methanol had a low of 201 ppm and a high of 1890 ppm. Formaldehyde was less than 75 ppm with one exception.

Carbon monoxide and dimethly ether are the most difficult compounds to convert completely. Data on these for the outlet condition was obtained for all runs from November through February. Carbon monoxide averaged 50.6 ppm while dimethyl ether averaged 96.5 ppm. It is interesting to note that variances from the average bear no relationship to inlet concentrations or flow conditions.

Although only six complete data points were obtained during the testing, the reasonably constant outlet concentrations of carbon monoxide and dimethyl ether and the latter information on formaldehyde and methanol indicate the catalytic incinerator has been operating in the range of 97.9% to 98.5% conversion of the exhaust pollutants over a one year period without change.

The results of the NOx testing indicated an inlet of 11 ppb and an outlet of 12.3 ppb. The background reading was 9 ppb. It is evident NOx is

TABLE 4. FULL-SCALE TEST DATA SUMMARY

Test Date	Flow Rate (m^3/h)	Outlet Temp. (^oC)	Removal Efficiency %				
			CO	CH_3OH	CH_3OCH_3	HCHO	Overall
11/30/79	4945	540	98.9	97.2	96.8	95.0	97.9
12/18/79	5149	532	99.1	98.6	97.2	98.6	98.5
1/11/80	2957	540	99.3	99.2	96.6	97.0	98.3
3/13/80	-	-	99.0	93.2	96.6	98.6	97.9
3/18/80	4124	505	99.0	98.9	96.7	99.1	98.3
3/25/80	4590	510	99.0	97.1	96.5	98.7	98.0

not being generated in the abatement system.

SECTION 5

ECOMONIC COMPARISON

The annual cost of operating an air pollution abatement system depends on the level of abatement required. Catalytic systems have been built to achieve effluents in the low part per trillion range as in trituim systems; however, in general, most abatement systems operate on a basis of removing 95%-99% of the pollutants. Both thermal and catalytic systems achieve these levels.

A good illustration of the difference in cost between a 95% and a 99% removal is thermally to compare residence time and catalytically to compare catalyst volume. Data presented by Rolke[2] indicates in a thermal unit the residence time at 99% removal would be approximately six times that at 95%. The catalyst volume which is calculated from the concentrations

$$\text{Catalyst Volume} \sim \ln \frac{\text{Inlet Concentration}}{\text{Outlet Concentration}}$$

would increase about 50 percent for the same removal efficiencies. Constant temperatures were assumed in both cases.

A second consideration in determining annual cost is a balancing of operating expenses with capital costs. The major capital cost item which influences operating cost is the heat exchanger. For low concentration hydrocarbon exhaust streams preheating the inlet stream with the outlet stream is most important. Heat exchangers which return 40% of the exhaust heat to the inlet gas represent approximately 30% of the material cost in building a system. Increasing the efficiency of the heat exchanger to 60% would double its cost.

An additional operating cost is the power consumed to move the exhaust through the abatement system. This becomes most critical in sizing heat exchangers and catalyst beds.

The economic comparison of a thermal and catalytic system presented

here is limited to a comparison of units with the similar efficiencies of operation, reduction of pollutants, and material costs. The capital and annual cost of operating an air pollution abatement system is shown in Table 5.

Capital Cost

The purchase cost of the catalytic units are based on construction techniques used in incinerator systems Engelhard has already sold. Updated costs of these units have been used to develop the purchase prices shown in Table 3. In order to obtain the closest comparision, the thermal units were estimated using the same construction techniques, the same burners, instrumentation, and type of heat exchangers. Blowers were not included in the estimates.

Flow schematics (Figures 11, 12, 13, & 14) are indicative of such type system. The units are completely skid mounted, prewired, and piped, ready to convert to the plant piping. Ductwork which is part of the unit (i.e., that included in the schematics) may be shipped separately, as well as the heat exchangers of the larger units due to shipping size limitations.

Annual Cost

An annual cost comparison depends on many factors. These factors vary in different areas and with the economic climate. The values shown in Table 4 are for comparison of catalytic versus thermal systems and should not be used as a basis for cost estimating a specific application.

The following assumptions were made in conducting the economic analysis:

1. See Table 6 for technical basis.
2. Installation costs are assumed to equal the purchase price.
3. Catalyst replacement is included on a three year basis. Test results indicate this as a minimum catalyst life.
4. Natural gas fuel at $.50 per therm.
5. Interest on capital, 10%.

TABLE 5. CAPITAL AND ANNUAL COSTS ($)

	PLASTIC PRINTING				FORMALDEHYDE			
	Catalytic		Thermal		Catalytic		Thermal	
Capacity (m^3/h)	16,992	33,984	16,992	33,984	8,496	16,992	8,496	16,992
Purchase	186,000	271,000	177,000	247,000	150,000	207,000	135,000	174,000
Installed	186,000	271,000	177,000	247,000	150,000	207,000	135,000	174,000
Capital Cost	372,000	542,000	354,000	494,000	300,000	414,000	270,000	348,000
Capital Recovery* (16.3%)	60,600	88,300	57,700	80,500	48,900	67,500	44,000	56,700
Catalyst Repl.	19,300	38,600	-	-	10,500	20,900	-	-
Maintenance(2%)	7,500	10,800	7,100	9,900	6,000	8,300	5,400	7,000
Fuel	36,500	73,000	107,500	214,000	-	-	198,000	370,000
Annual Cost	123,900	210,700	172,300	304,400	65,400	96,700	247,400	433,700

*Capital Recovery Factor of 16.3% is based on 10% interest over a 10 year period.

TABLE 6. COST COMPARISON FACTORS

PLASTIC FILM PRINTING SYSTEMS

Air inlet 21°C.
Dryer inlet 93°C.
Catalyst bed exhaust 315°C.
Thermal incinerator exhaust 760°C.
Gas BTU content causes 28°C rise.
Heat exchanger 41% efficient.
No thermal losses except to stack.
Heat exhanger catalytic - Corten steel.
Heat exchanger thermal - stainless steel.

FORMALDEHYDE SYSTEMS

Air inlet 21°C.
Catalyst bed exhaust 510°C.
Thermal incinerator exhaust 760°C.
Gas BTU content causes 289°C rise.
Heat exchanger 41% efficient.
No thermal losses except to stack.
Heat exchanger - stainless steel.

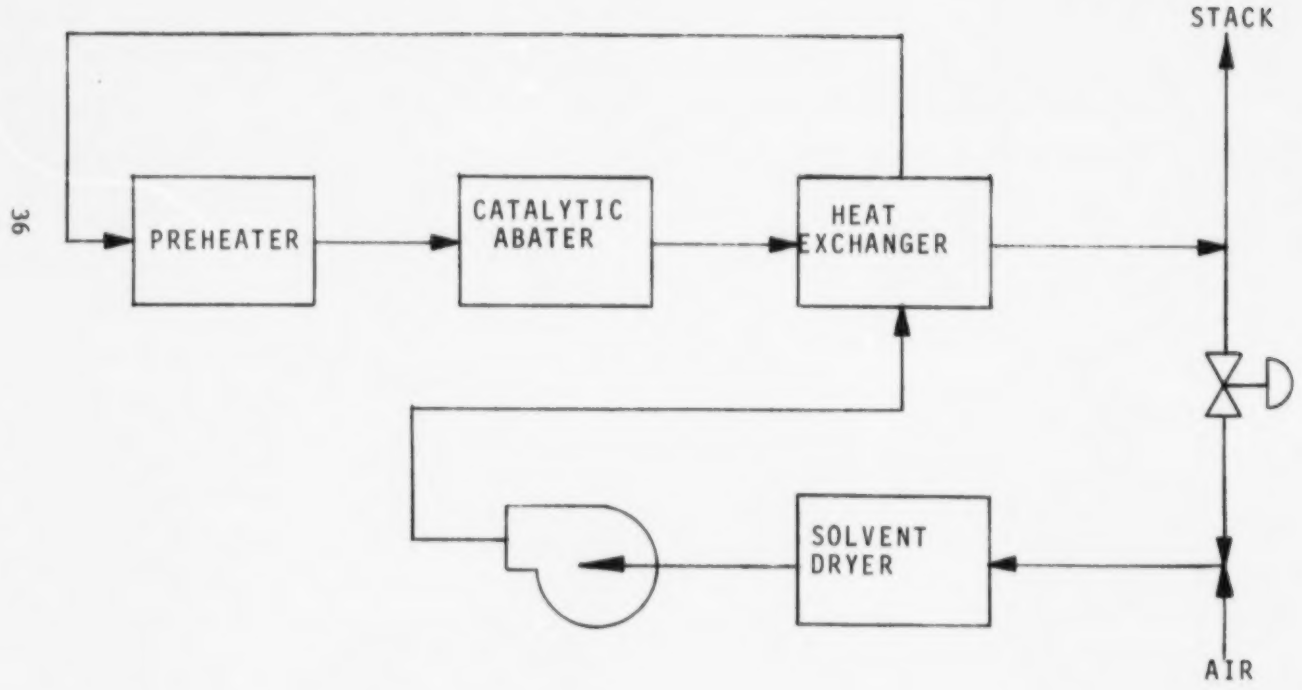


Figure 11. Flow Schematic. Plastic Printing Plant - Catalytic Abatement System

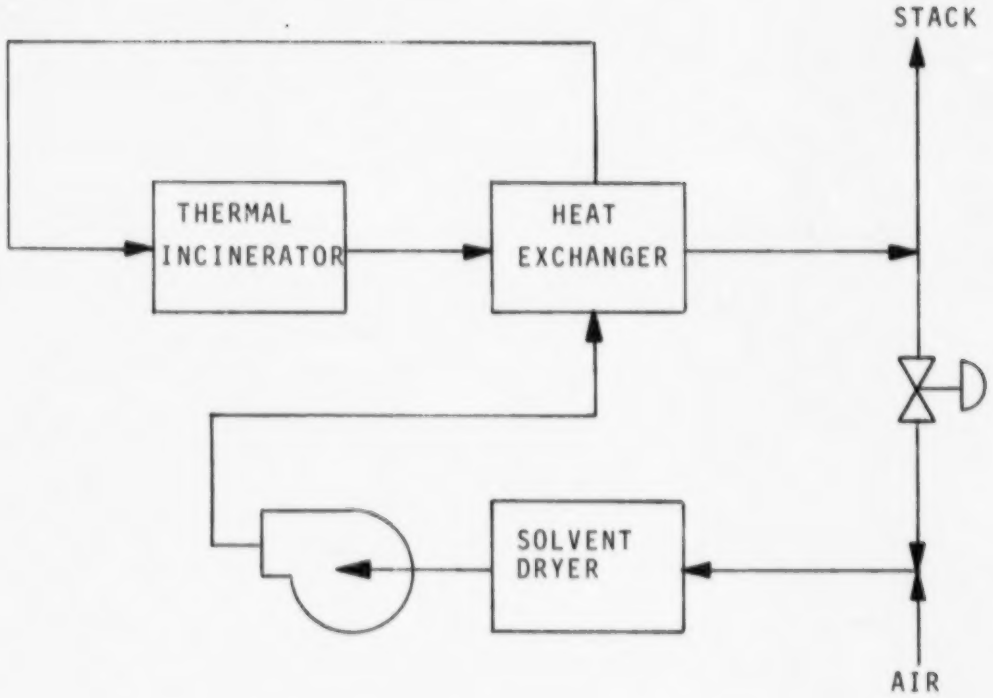


Figure 12. Flow Schematic. Plastic Printing Plant - Thermal Incinerator

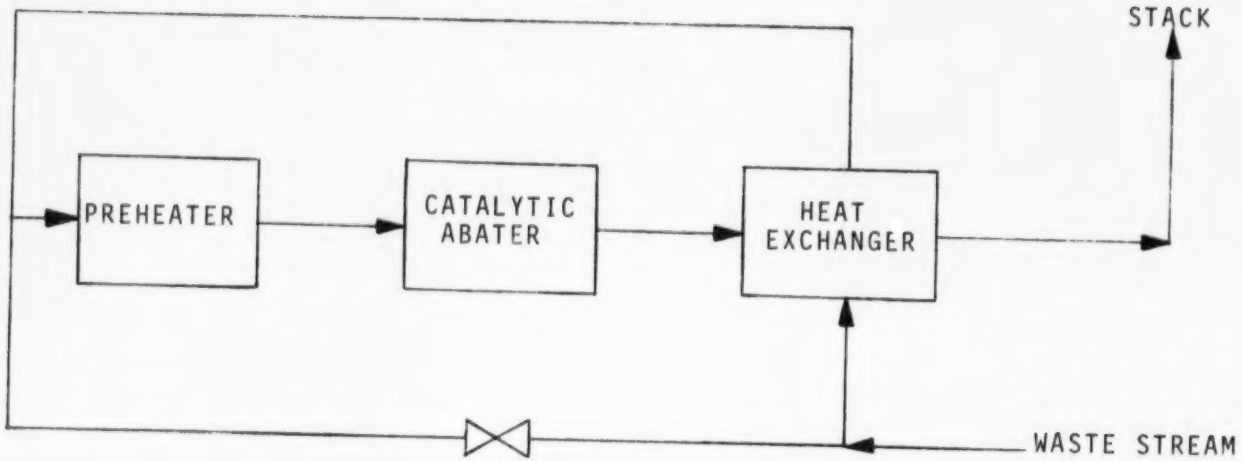


Figure 13. Flow Schematic. Formaldehyde Plant - Catalytic Abatement System

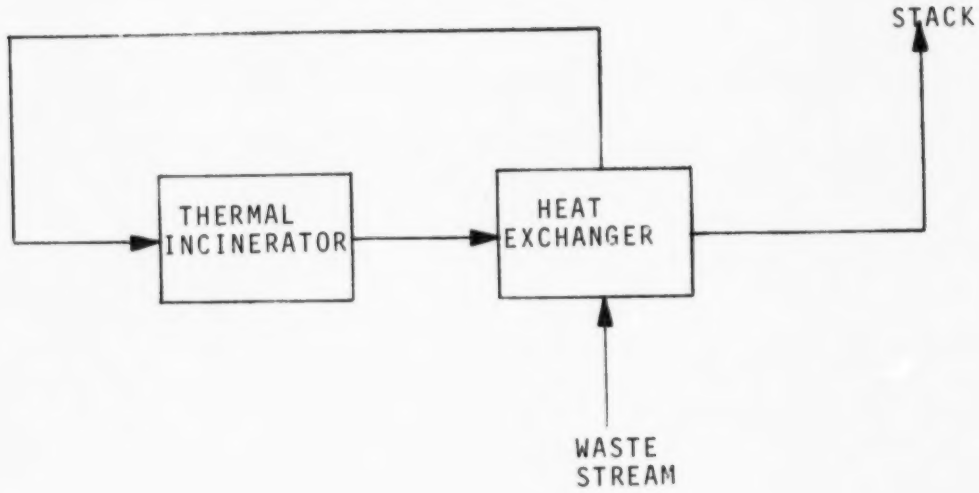


Figure 14. Flow Schematic. Formaldehyde Plant - Thermal Incinerator

REFERENCES

1. Trends, Pollution Engineering, Volume 10, Number 11, November 1978, 9 pp.

2. Rolke, R. W., et al. Afterburner Systems Study. EPA, EHS-d-71-3, Shell Development Company, Emeryville, California, pp 19.

3. Chemists Dictionary, D. Van Nostrand Co., Inc., New York, 1st Ed, 1953, pp 134.

APPENDIX A

PILOT UNIT TESTS

Table A-1: Preliminary Testing
Table A-2: Preliminary Testing
Table A-3: One Month Test
Table A-4: Two Month Test
Table A-5: Three Month Test
Table A-6: Five Month Test

TABLE A-1: PRELIMINARY TESTING

Date	7/17	7/17	7/17	7/17	7/17	7/17	7/17	7/17
Time	0929	1001	1030	1305	1400	1430	1500	1643
Measurement No.	1	2	3	4	5	6	7	8
Flow Rate(m^3/h)	8.3	11.9	15.3	14.6	11.9	8.5	5.1	5.1
Space Velocity x 1000	49	70	90	86	70	50	30	30
Catalyst Inlet Temp. (^oC)	371	371	371	316	316	316	313	260
Catalyst Outlet Temp. (^oC)	402	406	407	360	362	362	360	316
Catalyst Press. Drop (Pa)	622	846	1120	996	871	572	373	249
Inlet Analysis (ppm)								
Ethanol	374	374	374	466	469	456	464	456
N-Propanol	194	194	200	220	239	228	219	225
N-Propyl Acetate	11.2	11.2	13.4	20.0	24.0	27.0	34.0	33.0
Outlet Analysis (ppm)								
Ethanol	0.98	1.61	1.50	1.75	2.02	1.94	1.06	1.81
N-Propanol	0.41	0.61	1.30	1.97	1.89	0.85	0.26	9.84
N-Propyl Acetate	0.25	0.25	0.92	1.08	0.70	0.76	0.22	0.84

TABLE A-2: Preliminary Testing

Date	7/18	7/18	7/18	7/19	7/19	7/19
Time	1320	1352	1515	1021	1200	1115
Measurement No.	9	10	11	12	13	14
Flow Rate (m^3/h	11.9	8.5	5.1	5.1	8.5	12.2
Space Velocity	70	50	30	30	50	72
Catalyst Inlet Temp.(^oC)	266	291	277	338	346	340
Catalyst Outlet Temp.(^oC)	316	313	311	354	371	368
Catalyst Press Drop (Pa)	747	498	249	249	498	747
Inlet Analysis (ppm)						
Ethanol	250	247	254	274	279	277
N-Propanol	159	148	176	185	184	182
N-Propyl Acetate	7.3	4.5	4.5	4.5	4.5	4.0
Outlet Analysis (ppm)						
Ethanol	3.49	2.44	0.55	0.65	1.76	3.04
N-Propanol	2.04	1.11	0.12	0.45	0.73	1.63
N-Propyl Acetate	0.48	0.35	0.10	0.25	0.10	0.37

TABLE A-3: ONE MONTH TEST

Date	8/15	8/15	8/15	8/15	8/15	8/15	8/16	8/16	8/16
Time	1221	1301	1346	1542	1614	1642	1112	1138	1303
Measurement No.	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1
Space Velocity x 1000	70	50	30	70	50	30	70	50	30
Catalyst Inlet Temp.(°C)	327	327	333	230	232	227	285	288	282
Catalyst Outlet Temp.(°C)	365	368	368	260	260	260	316	316	316
Catalyst Press. Drop (Pa)	747	622	373	622	373	249	747	498	249
Inlet Analysis (ppm)									
Ethanol	489	466	404	443	459	405	488	509	510
N-Propanol	367	345	306	371	374	319	298	315	333
N-Propyl Acetate	30.3	36.5	33.4	36.2	30.0	24.6	27.7	26.1	24.5
Outlet Analysis (ppm)									
Ethanol	5.82	3.68	1.34	2.70	2.95	1.0	8.03	6.1	1.19
N-Propanol	3.80	1.98	0.65	7.6	3.45	1.06	10.5	6.9	1.2
N-Propyl Acetate	1.48	0.81	0.08	15.0	9.50	4.43	2.30	1.44	0.2

TABLE A-4: TWO MONTH TEST

Date	9/17	9/17	9/17	9/18	9/18	9/18	9/18	9/18	9/18
Time	1420	1445	1545	0925	0957	1005	1208	1253	1357
Measurement No.	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	12.1	8.5	5.1	11.7	8.5	4.9	11.7	8.5	5.1
Space Velocity x 1000	71	50	30	69	50	29	69	50	30
Catalyst Inlet Temp.(°C)	337	335	326	285	288	285	232	229	241
Catalyst Outlet Temp.(°C)	371	371	371	316	316	313	260	263	257
Catalyst Press. Drop (Pa)	747	809	373	747	498	249	622	373	249
Inlet Analysis (ppm)									
Ethanol	456	522	522	413	433	373	413	494	509
N-Propanol	458	448	461	346	362	346	346	365	371
N-Propyl Acetate	11.5	26.5	23.3	16.8	13.6	11.2	16.8	21.9	20.9
Heptane	1.3	32.5	20.9	8.4	4.5	3.5	11.8	20.0	17.8
Outlet Analysis (ppm)									
Ethanol	2.8	2.7	0.4	7.4	4.6	2.6	12.9	9.2	1.7
N-Propanol	1.15	0.39	0.33	7.4	4.2	2.0	10.4	10.4	0.8
N-Propyl Acetate	0.4	0.26	0.1	1.1	0.57	0.1	7.6	8.8	1.4
Heptane	0.04	0.89	0.5	1.0	0.72	0.07	7.7	8.4	1.3

TABLE A-5: THREE MONTH TEST

Date	10/10	10/10	10/10	10/11	10/11	10/11	10/11	10/11	10/11
No. of Samples Averaged	6	4	3	3	3	3	3	4	3
Measurement No.	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1
Space Velocity x 1000	70	50	30	70	50	30	70	50	30
Catalyst Inlet Temp.(°C)	337	337	327	279	285	271	238	230	232
Catalyst Outlet Temp.(°C)	371	371	362	316	316	316	266	260	260
Catalyst Press. Drop (Pa)	647	498	299	622	498	249	622	373	249
Inlet Analysis (ppm)									
Ethanol	474	492	503	458	450	429	382	389	431
N-Propanol	274	306	306	312	324	330	366	365	373
N-Propyl Acetate	29	27	31	26	30.2	32.3	20.4	14.5	10.4
Heptane	20.8	12.6	19.3	21.0	9.4	48	26	12.9	9.1
Total Organics	646	608	618	609	623	630	610	557	582
Outlet Analysis (ppm)									
Ethanol	8.2	4.4	1.0	12.8	8.9	1.1	16.4	9.5	1.5
N-Propanol	.1	.1	.1	11.5	7.2	0.6	18.3	10.3	1.3
N-Propyl Acetate	1.1	.1	.1	3.5	2.1	0.5	9.6	7.1	4.0
Heptane	*	*	*	3.5	3.4	1.1	11	4.9	2.0
Total Organics	15	12	12	35	31	30	106	79	73

*Not readable due to interference of background

TABLE A-6: FIVE MONTH TEST

Date	12/11	12/11	12/12	12/12	12/12	12/12	12/12	12/12	12/12
Time	1458	1615	1019	1117	1230	1318	1453	1515	1540
Measurement No.	1	2	3	4	5	6	7	8	9
Flow Rate (m^3/h)	11.9	8.5	5.1	11.9	8.5	5.1	11.9	8.5	5.1
Space Velocity x 1000	70	50	30	70	50	30	70	50	30
Catalyst Inlet Temp.(°C)	330	330	319	260	260	252	221	224	221
Catalyst Outlet Temp.(°C)	371	371	365	321	319	319	260	265	260
Catalyst Press. Drom (Pa)	560	436	249	498	249	249	436	324	199
Inlet Analysis (ppm)									
Ethanol	536	581	505	527	476	483	546	538	542
N-Propanol	250	297	253	273	288	287	303	305	310
N-Propyl Acetate	45	42	24.6	20.6	29.1	31.3	51.4	54.2	51.4
Heptane	*	*	38.1	28.0	15.0	27.0	29.0	24.6	21.7
Outlet Analysis (ppm)									
Ethanol	7.0	2.77	1.1	11.6	5.23	1.4	21.9	13.7	2.1
N-Propanol	3.5	1.41	0.45	7.47	3.6	0.7	13.6	7.77	0.77
N-Propyl Acetate	1.7	0.51	0.04	3.1	2.0	0.3	28.7	21.9	11.3
Heptane	*	*	0.38	4.12	1.22	0.45	22.0	12.2	5.0

* Operating Difficulty prevented analysis

APPENDIX B

FULL SCALE TEST

Table B-1: July - August Testing
Table B-2: September - October Testing
Table B-3: November - December Testing
Table B-4: January Testing
Table B-5: February - March Testing

TABLE B-1: JULY - AUGUST TESTING

DATE	INLET ANALYSIS				FLOW RATE (m^3/h)	INLET TEMP. (°C)	OUTLET TEMP. (°C)		OUTLET ANALYSIS			
	CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)					CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)
7/19	NA	91*	NA	NA	5386**	243	552			< 1	< 1	< 1
7/20	7300	91*	4260	260	5386**	233	538			< 1	60	< 1
7/24	6610	91*	4030	195	5081	228	523			< 1	58	< 1
7/27	NA	91*	2750	151	5318	229	527			< 1	54	< 1
7/31	4820	91*	3040	148	5200	238	538			< 1	58	< 1
8/03	3630	91*	2360	NA	5386	240	543			< 1	60	< 1
8/08	3910	91*	4930	163	5234	241	545			< 1	60	< 1
8/10	5220	91*	3450	209	5268	238	538			< 1	56	< 1
8/14	NA	91*	NA	NA	5217	224	515			< 1	74	< 1
8/17	6520	91*	4560	NA	5709	263	571			< 1	57	< 1

* Calculate valves based on concentration of formaldehyde in top tray
** Based on average air flow and average methyl alcohol flow for month of July

TABLE B-2: SEPTEMBER - OCTOBER TESTING

DATE	INLET ANALYSIS				FLOW RATE (m^3/h)	INLET TEMP. (°C)	OUTLET TEMP. (°C)		OUTLET ANALYSIS			
	CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)					CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)
9/07	6600	NA	2720	**	5318	232	515			< 1	53	< 1
9/11	5100	55	2200	**	5437	243	538			< 1	54	< 1
9/13	NA	NA	NA	**	5098	250	555			21	111	< 1
9/14	5100	287	1600	**	5251	266	538			< 1	86	< 1
9/17	NA	NA	NA	**	5149	232	527			< 1	< 1	< 1
9/26	NA	NA	NA	**	5471	260	515			< 1	46	< 1
9/27	4700	NA	2850	**	5132	232	527			< 1	< 1	< 1
9/28	2260	NA	NA	**	5251*	260	515			< 1	< 1	< 1
10/08	NA	NA	NA	**	5064	232	532			< 1	< 1	< 1

* Flow rate based on average of September's back pressure readings
** ppm MeOH estimated to be between 400 and 600
NA=Not Available

TABLE B-3: NOVEMBER - DECEMBER TESTING

DATE	INLET ANALYSIS				FLOW RATE (m^3/h)	INLET TEMP. (°C)	OUTLET TEMP. (°C)		OUTLET ANALYSIS			
	CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)					CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)
					4808	230	531		44	< 4	105	
11/06					5199	230	528		48	< 4	75	
11/09	3390	< 75	2480	1890	5437	238	538		62	< 4	75	
11/13	3750	< 20	2920	480	5267	232	530		48	< 4	76	
11/16	3700	< 75	2740	480	4945	240	538		55	< 4	80	
11/27	5050	< 75	2680	690	5200	240	540		44	< 4	78	23
11/30	4140	< 36	2420	461								
					4996	240	540		94	< 1	88	
12/11	3830	< 75	3135	330	5369	229	531		69	< 1	45	
12/14	4600	< 20	3520		5149	237	532		58	< 1	91	9
12/18	6440	72	3230	650								

TABLE B-4: JANUARY TESTING

DATE	INLET ANALYSIS				FLOW RATE (m^3/h)	INLET TEMP. (°C)	OUTLET TEMP. (°C)		OUTLET ANALYSIS			
	CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)					CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)
1/04	4820	< 20	3388	201	2940	255	540		34	< 1	106	
1/08	5350	< 55	3480	221	2991	258	544		42	< 2	120	
1/11	6100	263	3360	263	2957	255	540		40	< 2	115	8
1/15	8050		5150		3178	248	520		40		122	
1/18	5095		3185		3245	258	543		37		119	
1/22	4970		3290		5166	250	555		55		100	
1/25	6980		4200		5335	248	558		62		105	

TABLE B-5: FEBRUARY - MARCH TESTING

DATE	INLET ANALYSIS				FLOW RATE (m^3/h)	INLET TEMP. (°C)	OUTLET TEMP. (°C)		OUTLET ANALYSIS			
	CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)					CO (ppm)	HCHO (ppm)	DME (ppm)	MeOH (ppm)
2/01	5050		3230		5369	225	570		45		96	
2/05	5580		2470		4979	195	430		57		128	
2/08	4730		3860		5352	251	570		42		113	
2/20	5390		4480		4588	230	532		32		92	
2/22	5540		2950		4865	230	558		55		98	
3/13	4360	206	3340	436					43	14	113	6
3/18	4355	1490	3110	931	4124	212	505		44	16	103	8
3/25	4830	589	3090	476	4590	220	510		49	17	108	6

APPENDIX C

ANALYTICAL METHODS - PILOT UNIT TEST

TEST METHOD C-1

TEST METHOD C-1: METHOD OF TESTING EMISSION GASES FROM A PILOT CATALYTIC UNIT INSTALLED ON AN INK DRYER AT WARWICK, NEW JERSEY

1.0 SCOPE

This method covers the analyses of ethanol, n-propyl alcohol, n-propyl acetate, heptane and total organics in the air exhausting from an ink dryer before and after catalytic oxidation.

2.0 METHOD OF TEST

Gas chromatography with flame ionization detection. Calibration was accomplished with prepared standards of ethyl alcohol, proply alcohol, proply acetate, heptane, and hexane.

3.0 EQUIPMENT

Gas chromatographs (1) Carle Model 9700 and Varian Model 1200. Carle gas sampling valves, air moving pumps and accessory items. Supply gases for the operation of the gas chromatographs, air, hydrogen and nitrogen.

4.0 OPERATING PARAMETERS

Column Oven	100°C
Detector	150°C FID
Carrier	N_2 at 35cc/min.
Combustion Gas	H_2 30 cc/min,
Air	300 cc/min.
Column	FFAP 10 ft, 1/8" O.D.
Catalytic Incinerator Parameter	3-7 SCFM; Inlet 450°-650°F Outlet 500°-700°F, pressure of inlet and outlet will be 0-4" w.c.

5.0 OPERATING PROCEDURE

The samples of air to be analyzed are drawn to the gas sample valve through non-absorbing teflon tubing by pumps. On signal, the sample valves are switched and the analysis begun. Prepared gas standards are used for the calibration of both gas chromatographs. Calibration is to be made at the beginning and end of the testing for each day. The instrument output is recorded on a single 2-pen strip chart

recorder for ease of data comparison. The total hydrocarbon analysis is determined by sampling the vapors in the usual manner, then back-flushing all components to the detector for a measure of all components. The calibration is achieved with prepared hexane gas standards.

6.0 REPORTING

The data is in the form of chromatographic recordings which are analyzed by the area comparison technique with known samples and reported on data sheets. A total of nine (9) tests are run, each portraying three (3) different space velocities at three (3) different temperatures.

A minimum of three samples at each of these points are analyzed to verify identical recordings but only one set of recordings is reported. (Exception: the data for the three month test is an average of the three or more samples.)

APPENDIX D

ANALYTICAL METHODS - FULL SCALE TEST

TEST METHOD D-1

TEST METHOD D-2

TEST METHOD D-1

Method of Testing Emission Gases from
Engelhard Catalytic Unit Installed on
Formaldehyde Absorber Plant #2
Columbus, Ohio

1. SCOPE

1.1 This method covers the determination of carbon monoxide, formaldehyde, demethyl ether, and methyl alcohol in absorber emission gases leading into and exiting an Engelhard catalytic unit by using gas chromatography.

This method can determine gas concentrations from 2% by weight down to 1 ppm. The method utilizes external standards for CO, HCHO, $(CH_3)_2O$, and CH_3OH all in the gas phase.

2. SUMMARY OF METHOD

2.1 This method is intended for routine sampling and analysis of absorber emission gases. Directions are given for the collection of grab samples.

2.2 The gas analysis is performed in two parts each part using 0.5 ml samples. Carbon monoxide is analyzed by separation with a molecular sieve column. The remaining organic gases are separated on a Poropak T column.

Both columns are operated isothermally. The detector is a flame ionization type with a nickel reducing catalyst to methanate formaldehyde and carbon monoxide in order to enhance their detectability. All peaks are thus detected as methane.

3. SIGNIFICANCE

3.1 The measurement through monitoring emission gases prior to entering and after exiting the Engelhard catalyst unit provides data for assessing the effectiveness of the unit in reducing atmospheric pollutants emitted by the formaldehyde absorber.

4. APPARATUS

4.1 Gas chromatograph equipped for isothermal operation at up to 250°C.

4.2 Flame ionization detector with linear response characteristic for hydro carbons from 10 ppm to 10% by volume.

4.3 Six-port sample valves equipped with 0.5 scc sample loops.

4.4 Columns

4.4.1 Poropak T columns 1/8 inch OD stainless steel 22 feet in length packed with 100/120 mesh material which has been acetone washed and preactivated.

4.4.2 Mole sieve column 1/8 inch OD stainless steel 11 feet in length packed with 80/100 mesh water washed 5 X material which is preactivated at 310°C for 12 hours under helium flow.

4.5 Temperatures

4.5.1	Sample Valves	250°C
4.5.2	Detector	300°C
4.5.3	Injection Ports	150°C
4.5.4	Nickel Catalyst	350°C
4.5.5	Column Oven	145°C

4.6 Carrier gas is nitrogen, zero grade gas certified for total hydrocarbons as CH_4 to be below 0.5 ppm.

4.6.1 Mole sieve column flow rate 30ml/min
4.6.2 Poropak T column flow rate 30ml/min

4.7 Detector Gas

4.7.1 Hydrogen, Prepurified 99.95% H_2
4.7.2 Air breathing quality, clean, dry, and oil free

4.8 Standard Gases

Carbon monoxide and dimethyl ether standards in nitrogen obtained from M. G. Scientific Gases, Somerville, New Jersey.

4.8.1	Aluminum Tank #1	97.1 ppm CO
		19.6 ppm DME
4.8.2	Aluminum Tank #2	21.2 ppm Co
		20.1 ppm DME

4.9 Sampling Syringes

4.9.1 50cc Glass Syringes
4.9.2 50cc Disposable Plactic Syringes

4.10 Recorder: 10 inch wide strip chart recorded. A HP 7123A with 1 millivolt full scale sensitivity or its equivalent. Chart speed 4 inch per minute.

5. SET UP AND CALIBRATION

5.1 Gas Connections

5.1.1 Connect zero grade nitrogen up to carrier gas inlet on gas chromatograph. Set supply pressure to 100 psi.

5.1.2 Connect prepurified 99.95% hydrogen to F.I.D. fuel inlet to detector set supply pressure to 28 psi.

5.1.3 Connect air which is clean, dry, and oil free to F.I.D. oxidizer inlet to detector. Set supply pressure to 28 psi.

5.2 Connect 10 inch strip chart recorder to F.I.D. electrometer sensitive to 3×10^{-12} amps.

5.3 Connect columns to appropriate six-port sampling valves.

5.4 Install nickel catalyst tube between columns and detector.

5.5 Begin nitrogen flow through columns, catalyst tube and detector at 30ml/min ± 5ml per minute as measured with a soap film flow meter.

5.6 After purging system with nitrogen for 30 minutes set zone temperatures as follows:

Injection Ports	150°C
Column Oven	145°C
Sample Valves	250°C

5.7 When temperature of zones have stabilized check flow rate of columns and readjust to 30ml/min.

5.8 Begin hydrogen flow with head pressure of 28 psi. Check for flow.

5.9 Begin air flow with head pressure of 28 psi. Check for flow.

5.10 Shut off hydrogen and air.

5.11 Set temperature of remaining zones:

Nickel Catalyst Tube	350°C
Detector	300°C

5.12 When temperatures stabilize turn air and hydrogen on and ignite flame of F.I. detector.

5.13 Allow detector to equilibrate for 24 hours.

5.14 After 24 hour equilibration time turn recorder on and zero base line with electrometer controls.

• Drift of base line should be less than 1% per hour.

6. CALIBRATION

6.1 Calibration Standards

6.1.1 Carbon monoxide: CO -Certified calibration gases purchased from M. G. Scientific are used.

1% CO standard ± 0.01% for Inlet
100 ppm CO ± 1 ppm for Outlet
20 ppm CP ± 0.1 ppm for Outlet

6.1.2 Dimethyl ether: DME -Certified calibration gases purchased from M. G. Scientific are used.

1% DME standard ± 0.01% for Inlet
20 ppm DME ± 0.1 ppm for Outlet

6.1.3 Methyl Alcohol: MeOH

Reagent grade methyl alcohol purged with dry nitrogen at constant temperature to yield know concentration of MeOH in nitrogen gas sample.

500 ppm MeOH for Inlet
35 ppm MeOH for Outlet

6.1.4 Formaldehyde: HCHO

Formaldehyde concentrate 50% or 30% as analyzed by Sulfite method (See attachment #1).

Purge mixture of water containing known weight % HCHO with dry nitrogen at constant temperature.

150 ppm HCHO standard for Inlet
35 ppm HCHO standard for Outlet

6.2 Calibration Procedure - Bottled Gases

6.2.1 Purge sample loops with low flow of bottled calibration gases.

10 to 20 ml/min

6.2.2 Inject sample onto mole sieve column for carbon monoxide calibration.

6.2.3 Record peak height, width of peak at ½ peak height and retension time from injection, attenuation and range from electrometer. Adjust attenuation to maximize peak height while remaining on scale.

6.2.4 Calculate peak area by

Area = H x W

6.2.5 Calculate response factor for carbon monoxide.

$$RF_{co} = \frac{\text{ppm CO or \% from tank standard}}{H_{co} \times W_{co}}$$

6.2.6 Purge sample loops with bottled gas.

6.2.7 Inject sample onto Poropak T column for dimethyl ether.

6.2.8 Follow instruction given in steps 6.2.3 and 6.2.4 for DME.

6.2.9 Calculate response factor for dimethyl ether.

$$RF_{DME} = \frac{\text{\% or ppm DME from tank standard}}{H_{DME} \times W_{DME}}$$

6.3 Calibration Methyl Alcohol

6.3.1 Set up gas scrubber containing 500 ml reagent grade methyl alcohol.

6.3.2 Purge system with dry nitrogen 20 to 30 ml per minute.

6.3.3 Flush 50cc syringe with flow from scrubber saturated with methyl alcohol record temperature of vapor. Fill syringe with vapor.

6.3.4 Purge sample loops with vapor in syringe.

6.3.5 Inject sample onto Poropak T.

6.3.6 Follow instructions given in steps 6.2.3 and 6.2.4 for methyl alcohol.

6.3.7 Calculate % for methyl alcohol in vapor.

$$\% \text{ MeOH} = \frac{\text{partial pressure MeOH} \times 100}{\text{atmospheric pressure of day (or 760mm)}}$$

Partial pressure MeOH = Antilog of the $\log_{10} P$

$$\text{Log}_{10} P = \frac{0.05223 \times 38{,}324}{T°K} + 8.8017$$

6.3.8 Calculate response factor for MeOH.

$$RF_{MeOH} = \frac{\% \text{ MeHO}}{H_{MeOH} \times W_{MeOH}}$$

6.4 Calibration Formaldehyde

6.4.1 Prepare a solution of known weight % formaldehyde in water. Analyze a portion of this solution by attachment #1 procedure.

6.4.2 Place solution prepared in step 6.4.1 into gas scrubber and purge slowly with nitrogen as in step 6.3.1.

6.4.3 Flush 50cc syringe with HCHO saturated nitrogen, record temperature of solution.

6.4.4 Fill 50cc syringe with nitrogen from gas scrubber saturated with HCHO

6.4.5 Flush sample loops and inject sample onto Poropak T column.

6.4.6 Record retension time, peak height and peak width. See steps 6.2.3 and 6.2.4.

6.4.7 Calculate % formaldehyde in nitrogen vapor.

$$\% \text{ HCHO} = \frac{\text{partial pressure HCHO} \times 100}{\text{atmospheric pressure of day in mm}}$$

Partial pressure HCHO_{mm} = antilog of the $\log_{10} P^{mm}\text{HCHO}$

$$\text{Log}_{10} P^{mm}\text{HCHO} = 9.942 - 0.953\ (0.488)\ W/10 - \frac{2905}{T}$$

W = HCHO concentration in percent by weight

T = absolute temperature °Kelvin

6.4.8 Calculate response factor for HCHO.

$$RF_{HCHO} = \frac{\% \text{ HCHO}}{H_{HCHO} \times W_{HCHO}}$$

6.4.9 Limits of step 6.4.7.

Temperature is to be below 60°C for all concentrations and for temperature between 60° and 100°C applies only to concentration below 20% by weight.

6.5 The response of a hydrogen flame ionization detector is linear from 0.01 ppm to 10 ppm for C_1 through C_5 paraffinic and olefinic hydrocarbons. It is assumed the linear range for CO, DME, MeHO, HCHO is linear form 10 ppm to 10,000 ppm (1%) due to the presence of the nickel catalyst tube with a 0.5 scc sample loop.

7. PROCEDURE

7.1 Sampling of Gases

7.1.1 Grab samples are taken of all gas samples.

7.1.2 Fill 50cc syringe with gas to be samples and flush out syringes.

7.1.3 Fill syringe with sample gas and return to lab for analysis.

7.2 Location of Sampling Point

7.2.1 Engelhard Inlet samples are taken from the bottom of the formaldehyde absorber demister tank.

7.2.2 Engelhard Outlet samples are taken from the bottom of the Engelhard Catalytic Unit.

7.3 Running Samples

7.3.1 Mark recording chart with date, name of sample (Inlet or Outlet) sample type CO or DEM, HCHO, MeOH.

7.3.2 Flush sample loops with sample. See steps 7.1.1 through 7.1.3.

7.3.3 Inject sample for CO onto mole sieve.

7.3.4 If attenuation must be adjusted to keep pen on scale resample.

7.3.5 Inject sample for DME, HCHO, and MeOH onto Poropak T column.

7.3.6 If attenuation must be adjusted to keep pen on scale resample.

7.3.7 Record peak height and width according to procedure outlines in steps 6.2.3 and 6.2.4.

8. CALCULATIONS

8.1 The concentration of each gas in the chromatograph is determined from the response factor for the gas as determined in the calibration section part 6.

8.2 ppm CO = $H_{CO} \times W_{CO} \times RF_{CO} \times$ Range x Attenuation

8.3 ppm HCHO = $H_{HCHO} \times W_{HCHO} \times RF_{HCHO} \times$ Range x Attenuation

8.4 ppm DME = $H_{DME} \times W_{DME} \times RF_{DME} \times$ Range x Attenuation

8.5 ppm MeOH = $H_{MeOH} \times W_{MeOH} \times RF_{MeOH} \times$ Range x Attenuation

9. AIRFLOW

9.1 Record Inlet temperature of air to Engelhard Catalyst unit in °Fahrenheit.

9.2 Record Outlet temperature of air from Engelhard Catalyst unit in °Fahrenheit.

9.3 Record methyl alcohol flow rate in gallons per minute to formaldehyde plant #2.

9.4 Record O_2 percentage of air flow to formaldehyde plant #2.

9.5 Determine SCFM air flow through formaldehyde plant #2.

Record back pressure in psi for plant #2 blower and then refer to Chart #1.

9.6 Determine SCFM air flow across Engelhard Catalyst bed. Revised 1/18/80.

$$V_{AF} = AF_{SCFM} \frac{(4727.9-(43.001)(\%O_2 in)}{3844.2+\frac{(AF)}{(MeOH_{GPM})}} \frac{}{(^{2}25.961)-(1.2633)(\%O_2 in)} - 34.039\frac{(MeOH)}{GPM}$$

AF_{SCFM} = Air flow to formaldehyde catalyst plant #2

$\%O_2$ = Oxygen percentage in air flow to formaldehyde catalyst plant #2

10. REPORTING

'0.1 Compile data for each month on attached form. Form #1.

10.2 Each day's data should contain the following:

Date

ppm CO		ppm Co	
ppm HCHO	Inlet	ppm HCHO	Outlet
ppm DME		ppm DME	
ppm MeOH		ppm MeOH	

Flow Rate MeOH
Inlet Temperature °F
Outlet Temperature °F

ATTACHMENT #1

GPAM 100.1
Issued 4/1/77

DETERMINATION OF FORMALDEHYDE CONTENT (SODIUM SULFITE METHOD)

SCOPE:

This method is for the determination of formaldehyde content of aqueous solutions of formaldehyde.

PRINCIPLE:

This method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite to form the formaldehyde-bisulfite addition product.

APPARATUS AND REAGENTS:

a. Analytical balance.
b. 2 ml volumetric pipet
c. 250 ml iodine flasks
d. 50 ml buret
e. 1M sodium sulfite. Dissolve 126 g Na_2SO_3 (anhydtous) in about 950 ml distilled water. Add a few drops of thymolphthalein indicator and neutralize. Make up 1000 ml. This solution should be made frequently in small quantities to avoid loss of strength due to oxidation. Solution over three weeks old should not be used.
f. 1N sulfuric acid. Standardize as follows:
   1) dry reagent grade Na_2CO_3 for 1 hour at 270-300°C. Cool in desicator.
   2) weigh, by difference, triplicate samples of 2g each within ± 0.2 mg and transfer quantitatively to 250 ml flasks.
   3) dissolve each sample in 50 ml distilled water.
   4) titrate with the acid to be standardized to pH 5.0 or to methyl orange end point.
   5) titrate a blank of 50 ml distilled water in the same manner as 4.
   6) calculate normality as follows:

$$\text{Normality} = \frac{\text{WEIGHT OF } Na_2CO_3 \times 1000}{(\text{Av. ml titrant for } Na_2CO_3 \text{ solution} - \text{ml titrant for blank})\ 53.00}$$

g. Thymolphthalein indicator. Dissolve 0.1 g thymolphthalein in 100 ml
h. 0.1 N NaOH

PROCEDURE:

a. Place 25 ml distilled water in a 250 ml iodine flask and add 5 drops of thymolphthalein indicator.
b. Weigh the stoppered flask to the nearest 0.001 g.
c. Add a 2 ml formaldehyde sample, keeping the pipet tip below the water surface.
d. Immediately restopper the flask and reweigh to the nearest 0.001 g.
e. Neutralize the solution with 0.1 N NaOH.
f. Add 75 ml of 1 M Na_2SO_3 solution, this solution being first added around the stopper which is lifted to allow a portion to enter the flask. This procedure should prevent the loss of formaldehyde.
g. Mix thoroughly and titrate the liberated NaOH with 1 N H_2SO_4 until the blue color just disappears.
h. Run a blank in the same manner using the same amounts of reagents, adding water to match the total volume of the titrated solution.

CALCULATION:

$$\text{Wt. \% formaldehyde} = \frac{(\text{ml acid used} - \text{ml acid in blank})(\text{N of acid})\ 3.003}{\text{weight of sample}}$$

INTERPRETATION:

Formaldehyde solutions sold by Georgia-Pacific Chemical normally range from 37-50% formaldehyde content.

DATE	INLET ANALYSIS				FLOW RATE SCFM	INLET TEMP. °F	OUTLET TEMP. °F	OUTLET ANALYSIS			
	PPM CO	PPM HCHO	PPM DME	PPM MeOH				PPM CO	PPM HCHO	PPM DME	PPM MeOH

ADDENDUM

ITEM #1 Please note that the statement regarding the ability of the nickel catalyst to methanate formaldehyde quantitatively in Section 2.2 has not been documented by laboratory personnel nor are specific references detailing this step available to the laboratory at this time.

ITEM #2 Regarding Inlet and Outlet levels for carbon monoxide Section 6.1.1, dimethyl ether Section 6.1.2, methyl alcohol Section 6.1.3, and formaldehyde Section 6.1.4 these values are based on information contained in a memo to R. C. Moehl from N. Magnussan dated March 14, 1978.

ITEM #3 Regarding Section 1.1 and Section 6.5 dealing with dynamic linear range of the detector these are estimates based on Ken Dunder's experience and not documented in any report at this time.

ITEM #4 Regarding Section 6.4.7 the equation for the vapor pressure of formaldehyde is taken from Walker's work on formaldehyde 3rd.ed., Pages 114 and 115.

ITEM #5 Regarding Section 6.3.7 the equation for the vapor pressure for methyl alcohol is taken from an undated memo by Barbara Richard. No references are given.

ITEM #6 Regarding Section 9.6 the equation to determine the volume of air flow across the Engelhard catalyst bed is taken from calculations performed by Tom Moehl in an undated memo based on equations supplied by Al Buckingham in a memo to Ken Dunder dated May 18, 1979. No references are given.

ITEM #7 Regarding frequency of sampling please refer to the following letters:

To: Ken Dunder From: Norm Martin, Engelhard Industries
Dated: May 30, 1979 Test Specifications: TS-34

To: Norm Martin From: Ken Dunder, Georgia-Pacific Corporation
Dated: June 6, 1979.